SCHOOL OF CIVIL ENGINEERING

INDIANA DEPARTMENT OF HIGHWAYS

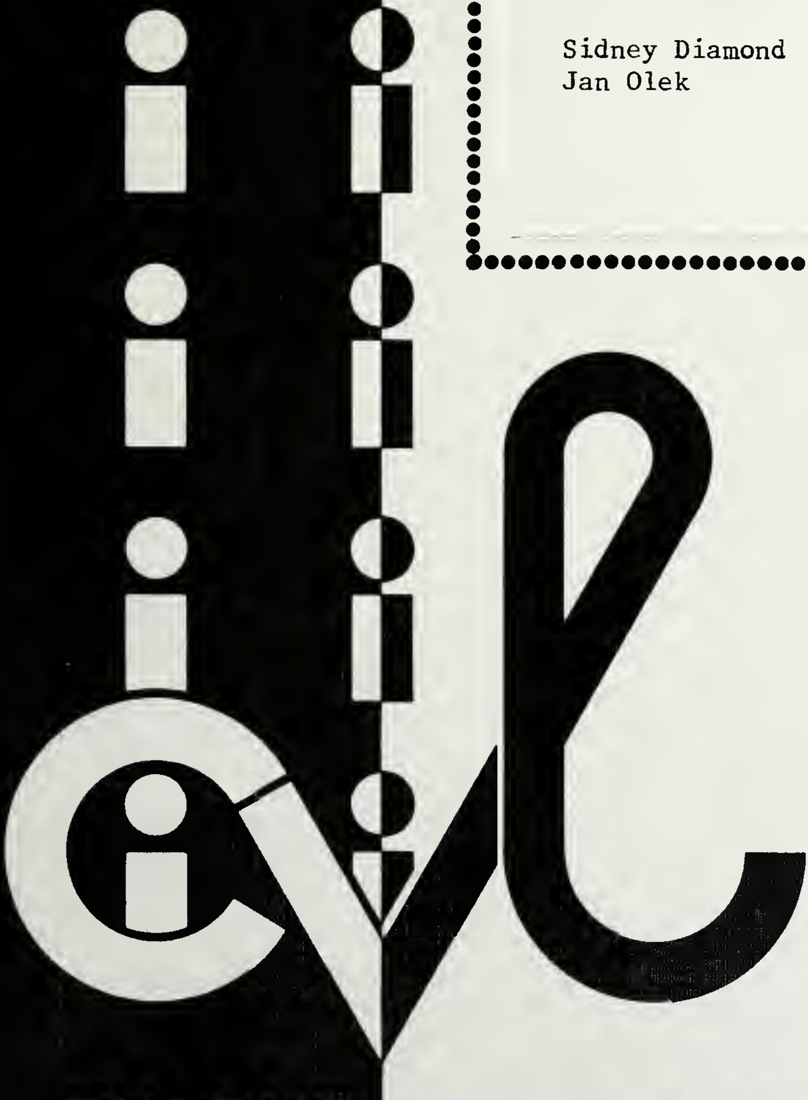
JOINT HIGHWAY RESEARCH PROJECT

FHWA/IN/JHRP-88/8 -1

Final Report

FLY ASH CONCRETE FOR HIGHWAY USE

Sidney Diamond
Jan Olek



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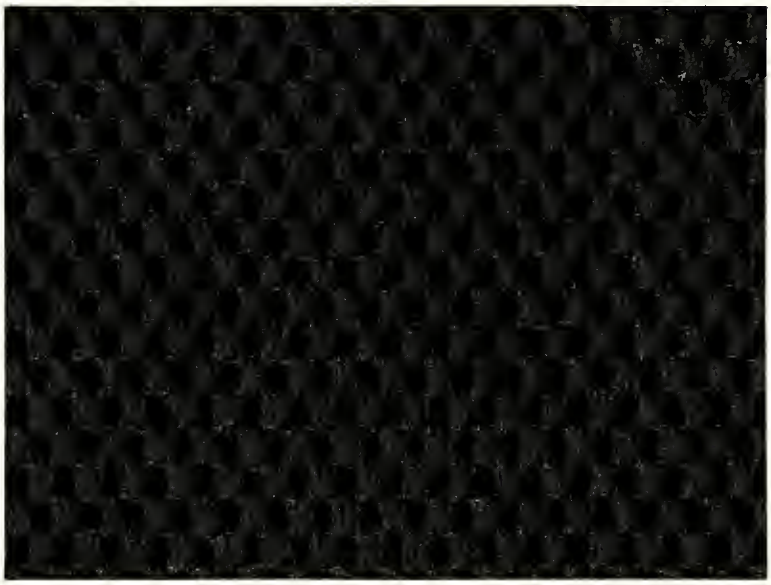

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Final Report

FLY ASH CONCRETE FOR HIGHWAY USE

TO: H. L. Michael, Director
Joint Highway Research Project
Mar. 24, 1988

FROM: S. Diamond, Research Associate
Joint Highway Research Project
Project: C-36-19G
File: 5-5-7

Attached is the Final Report of Phase II of the HPR Part II Study titled "Selection and Use of Fly Ash For Highway Concrete." The report is entitled "Fly Ash Concrete for Highway Use" and is authored by Professor Sidney Diamond and Dr. Jan Olek.

The objectives of the Study were accomplished. An appropriate new method of mix design of fly ash concrete for highway purposes was developed, and the properties and behavior of approximately 150 batches of concrete studied, along with studies on reactions in the paste components. It appears that properly-designed fly ash concretes should be entirely suitable for routine use for highway purposes, with benefits in economy, durability, and long-term strength.

A set of recommendations and guidelines for practical application has been included.

This Final Report is forwarded for review and acceptance by all sponsors as fulfilling the objectives of the study. With its approval and subsequent publication the Phase II referenced HPR study will have been completed.

Sincerely,

S. Diamond

Sidney Diamond
Research Associate

cc:

GRISSOM HALL • WEST LAFAYETTE, IN 47907

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16. Abstract

A series of investigations were carried out to examine the potential for routine use of fly ash in highway concrete, with special reference to Indiana. Existing methods of mix proportioning of fly ash concretes were reviewed in detail, and a new method developed to better assure good durability characteristics despite expected fluctuations in fly ash properties. Extensive investigations were carried out on the properties of concretes designed by this method and using representative Indiana fly ashes of both Class F and Class C varieties. In general these concretes exhibited compressive strengths and other mechanical properties at least as satisfactory as those of presently specified plain portland cement concretes, and the potential durability appeared to be significantly improved. The development of early flexural strengths was found to lag those of plain concretes somewhat, but after several months this lag disappeared. Provision of an adequate air content is necessary to assure freeze-thaw durability, and it was found that the necessary dosage of air entraining agent varied with the fly ash, but could be determined very easily by use of the foam index test. A number of technical conclusions were drawn with respect to reactions within the fly ash concretes, and a chapter on recommendations and cautions has been supplied.

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FLY ASH CONCRETE FOR HIGHWAY USE

by

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Project No.: C-36-19G
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for

Indiana Department of Highways

and

Federal Highway Administration
U.S. Department of Transportation

This research was carried out by the Joint Highway Research Project, Purdue University, under the direction of the first author as principal investigator. The contents do not necessarily reflect the official views or policies of the Indiana Department of Highways or the Federal Highway Administration. The report does not constitute a standard specification or regulation.

Purdue University
West Lafayette, IN 47907

March 24, 1988

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The support of this project by the Indiana Department of Highways (IDOH) and the Federal Highway Administration (FHWA) is gratefully acknowledged.

A number of people have contributed materially to this work. Miss Carol L. Kilgour, Mr. Qizhong Sheng, and Mrs. Janet Lovell have carried out a number of the determinations, and Mr. Joe Walters has been of great assistance in concrete laboratory studies. Mr. Patrick Hickner and Mr. William Freygang, undergraduate student assistants, provided assistance in preparing and testing concrete specimens.

We especially thank Mr. Richard Smutzer and his associates at the IDOH Division of Materials and Tests for carrying out the freezing and thawing tests reported here, and for advice with selection of representative materials for this investigation.

The Study Advisory Committee for this project included Mr. Smutzer, and Messrs. L. D. Tucker and Keith Herbold of FHWA. We are grateful to these gentlemen for their significant contributions.

HIGHLIGHT SUMMARY

The objectives of this program were to study the details of the performance and behavior of concrete produced with fly ashes for potential use in highway concrete in Indiana.

In this work, after a thorough review of methods of mix proportioning for fly ash concretes, it was decided that existing methods would probably not guarantee performance of field highway concrete from the durability standpoint, in the face of expected major variations in fly ash quality and properties from job to job. A new method of mix proportioning was developed to address this need, and has been used to design all of the concrete studied in this project. Approximately 150 batches of concrete were produced, designed according to existing IDOH criteria, and including five representative Indiana fly ashes of both the Class C and Class F types. In preliminary investigations it was found that the specific fly ash affected the dosage of air entraining agent needed to assure freezing and thawing resistance, but that the actual dosage needed could quickly be estimated from a simple foam index test procedure, easily carried out in the field.

It was found that the mix design method, properly applied, provided for very consistent control of slump and air content, regardless of specific fly ash used and replacement level. At a given slump level the fly ash concretes exhibited superior handling characteristics and reduced VeBe times.

All of the fly ash concretes were somewhat retarded with respect to set, and concrete made with one fly ash was sufficiently retarded that use of an accelerating admixture would probably be required in practice. All of the fly ash delayed and reduced the heat build up in early hydration.

Young's moduli and Poisson's ratio were measured for the fly ash concretes and were found to be closely correlated to each other and to compressive strength, but the relationships were quantitatively different than with plain concrete. The dynamic modulus of elasticity was initially lower for fly ash concretes but subsequently generally exceeded those of plain concrete. The compressive strengths of the fly ash concretes were found to be generally similar to those of the reference plain concretes at early ages; by 90 days many of the fly ashes produced substantially higher strengths. Somewhat lower flexural strengths were generally recorded at early ages, but these at least approached the values for plain concrete after several months.

Fly ash concretes were found to have potentially better durability characteristics than plain concrete; the pore structures determined by mercury porosimetry were finer, and chloride permeability measurements showed significantly lower chloride permeability. Freezing and thawing test results were highly favorable. Pore solutions were found to have decreased levels of alkalies, providing additional protection against possible alkali-aggregate reaction. It was found that the presence of the fly ashes augmented the capacity of the cement to fix much of the dissolved chloride, thus providing additional protection with respect to chloride induced steel corrosion. The additional capacity to fix chlorides may also be beneficial in slowing the rate of chloride penetration through concrete from de-icing salt.

Studies of the reaction actually taking place within the fly ash cement systems disclosed surprisingly that very little pozzolanic reaction had taken place with any of the fly ashes used, even as late as one year; this suggests that the benefical effects produced by the fly ash were mostly derived from mechanisms other than pozzolanic reaction. One of these mechanisms was thought to be the stimulation by the fly ashes of increased hydration of the portland cement itself.

In general it was indicated that properly designed fly ash concrete would be entirely suitable for routine use in highway concrete even in the face of variations in fly ash quality, and could provide significant benefits in long term strength and durability properties. A set of specific practical recommendations and cautions was provided.

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1.0 INTRODUCTION

1.1 Overall Features of The Project

This report is the result of a research project formally designated "Selection and Use of Fly Ash for Highway Concrete: Phase II". As its name indicates, the project is a successor to an earlier research project "Selection and Use of Fly Ash for Highway Concrete" which was carried out between 1983 and 1985. The final report of the earlier project is available as Joint Highway Research Project Report FHWA/IN/JHRP-85-8, School of Civil Engineering, Purdue University.

The earlier project was focussed on an in-depth study of the properties of fly ashes sampled from 14 sources within and near Indiana. These fly ashes were tested in great detail to provide information on the specific ashes and to provide background on the range of properties to be expected for fly ashes potentially available for use in highway concrete in different parts of the state. The highlight summary of the final report of that project is provided in the following section of the present report.

In the present study, the focus was shifted from the study of fly ash properties to the study of the effects actually produced by different fly ashes in practical concrete, i.e. concrete specifically designed to be appropriate for highway pavements and structures under existing IDOH specifications.

Within this general context, the scope of the investigations carried out was wide. In addition to the study of fly ash effects on the parameters normally important in concrete technology, more fundamental studies of materials properties evaluated from a materials science viewpoint were also undertaken, and several lines of investigation on fly ash properties from the earlier project were pursued further to attempt to add to the base of fundamental information on fly ash characteristics.

In studying the effects produced by fly ashes in concrete, it is important to appreciate that the effects measured are interactions between the specific cement, the specific fly ash, and the specific mix design process employed to design the concrete.

In this project, concretes containing five different Indiana fly ashes were studied in depth. Four of the fly ashes were drawn from the sources investigated in the earlier project, although the material used, sampled in 1985, is not the same as the material used in the earlier project sampled in 1983. One new fly ash was included, from the Rockport Station of the Indiana and Michigan Electric Co. in the southwestern part of the state. This generating station is new, and produces an excellent Class C fly ash that is now widely used in concrete around the state.

Two different ASTM Type I portland cements widely used in Indiana were selected for use with the assistance of the Indiana Department of Highways; in the body of this report, it will become apparent that the influence of a given fly ash depends considerably on the particular cement it is employed with.

Finally, the matter of the mix design and the mix design process has received great attention. After a comprehensive review of the existing methods for mix design of fly ash-bearing concrete, it was decided that none of them meet a major particular objective of this study, that of assuring good performance of field concrete despite expected major variations in sources and properties of fly ash actually delivered to the job. Accordingly, a new method of concrete mix design was developed to better meet these specific needs. This new method is designated the "constant paste quality" or CPQ method, and it has been used to design all of the experimental concrete studied.

1.2 Highlight Summary of the Results of the Previous Project

The predecessor project was designed to provide a basic understanding of the potential sources of fly ash available for use in highway concrete in the state of Indiana.

A relatively large number of coal-burning power plants exist in Indiana since there are no active nuclear or hydro power facilities. Their locations are not uniformly distributed however; there are many plants in the coal-mining regions of southern Indiana and along the Ohio River, but essentially no sources of fly ash in northeastern Indiana.

A total of 14 fly ashes were collected, including twelve from within the state and two from southwestern Michigan that are marketed commercially in northeastern Indiana; the assemblage provided reasonable coverage of the state. The plants sampled ranged in size from 45

MW to over 2500 MW rated capacity, and included at least one from each of the five operating utilities in the state.

The fly ashes were examined in great detail using both standard and a number of special characterization methods. The color of each fly ash was determined according to the standard Munsell color naming system. Chemical methods included total chemical analyses, carbon analyses by the LECO method, and analyses of soluble alkalies and sulfates. Particle size distributions were determined and plotted graphically, along with measurement of mean particle size and percentage larger than 45 µm. Surface areas were measured in several different ways, as were the specific gravities of the fly ashes. The contents of the magnetic particles of each ash were measured, and x-ray diffraction analysis was carried out both for the whole fly ash and for the separated magnetic fraction. Scanning electron microscope characterization of each ash was provided. The pozzolanic activity index with cement was determined for each fly ash by both the standard method and a modified method.

All but two of the fly ashes were Class F low calcium materials. Most had very similar chemical characteristics which reflected their derivation from fairly uniform Illinois Basin coals; four were significantly different in chemistry. The fly ashes derived from Illinois Basin coals had high iron contents, and correspondingly high percentages of magnetic particles. The magnetic fractions generally were composed of components that are not reactive with cement, and should be classed as additions to the fine aggregate rather than as replacements for the cement.

The carbon contents of the fly ashes examined covered a wide spectrum, from less than 0.5% to about 9%. Particle size distributions also varied considerably; the finest fly ash had a mean size of only 3µm, the coarsest 78µm.

The two Class C fly ashes tested were both of high CaO contents (ca. 30%), but differed from each other in a number of properties.

Most of the fly ashes would seem to be at least marginally useful in concrete; one apparently highly superior ash and one very coarse ash that would be virtually useless in concrete were also among the collection.

In carrying out this work, new methods of determining the content of magnetic particles, of mounting fly ash for scanning electron microscopy examination, and of displaying particle size distributions were developed that should be of general utility.

1.3 Scope and Specific Objectives of the Present Research

The primary objective of this study was to determine the effects produced by representative Indiana fly ashes on the concrete mixes designed to be appropriate for highway pavements and structures. Specifically, the study evaluated the effects of these fly ashes on workability, strength gain, and durability related parameters such as freezing and thawing resistance and the relative chloride ion permeability. Tests related to sulfate attack susceptibility were not included since sulfate attack has not been reported in highway pavements in Indiana.

A secondary objective was to establish information for guidelines to be followed by the field engineer, in the form of (a) mix design procedures, and (b) materials related information needed to ensure good quality and durable fly ash concrete for highway applications. The resulting data are meant to supplement present material specifications and existing mix design procedures.

A third objective was to contribute to the fundamental knowledge of fly ash materials and their reactions in concrete.

Since the pioneering work of R.E. Davis and his associates on portland cement concretes containing fly ash in 1937 [1], much time and effort have been devoted to evaluating the effects of the fly ash on concrete properties and behavior.

While much of this research has been repetitious, the repetition is partially justified by the nature of fly ash itself. No two fly ashes are alike because the composition and properties of a fly ash reflect a) the composition of the specific coal being burned, b) the fineness to which the coal is ground in preparation for combustion, and c) the details of the design and operation of the combustion and ash collection system used. Even the fly ash from a single source can have quite variable characteristics depending on whether coal is burned from more than one source, the age of the plant and the operating conditions and procedures.

Since fly ashes are variable by-products of coal combustion processes and not themselves specifically manufactured, fly ashes are significantly more variable in composition than portland cements. Doubts about uniformity of composition raise doubts about uniformity of performance.

More quantitative knowledge is therefore needed about factors affecting the performance of fly ashes in concrete so that one can predict the effects of changes in particular fly ash characteristics on the properties of concretes. Unfamiliarity with the effects produced by fly ash in concrete, combined with inappropriate selection of the fly ash to be used in a particular job, may lead to performance problems of fly ash concrete.

Despite this, the use of fly ash as a component in concrete has become increasingly widespread in recent years, especially in ready mix concrete for general construction purposes. Unfortunately, highway pavements and other structures provide a much more severe environment for concrete than does conventional building construction or even most applications of mass concrete. Appropriate selection of fly ash to be used, and appropriate methods of mix design specifically geared to insure long-term satisfactory performance of highway concrete in severe environments are needed, since the properties of fly ash may be highly variable. Ignorance of these variations and an attempt to use fly ash without appropriate quality control can lead to poor quality concrete with low durability.

There is thus a need for a systematic procedure for producing fly ash concrete from locally available fly ashes that can be used to produce high quality concrete regardless of such variations.

This research program was designed to produce the information and procedures required to attain this end, with special reference to concrete for highway pavements and structures in Indiana.

In this work approximately 1100 concrete specimens, representing 150 different batches of concrete were made and tested. Mixing procedure, aggregate type, and slump were kept constant in the course of the investigations, and the influence of the following specific variables have been studied:

- fly ash type and content
- cement type
- content of air-entraining agent and its effectiveness
- mixing water and aggregate demand
- length of curing

All of the concrete mixes were air entrained, using a commercial air-entrainig agent representative of those used locally.

Among the parameters measured for all of the concretes were:

- slump;
- VeBe time;
- air-entraining agent requirements for each specific fly ash combination as measured using the foam index test;
- actual air content measured with a standard pressure meter;
- times of initial and final set of concrete;
- times of initial and final set of cement - fly ash paste of the same water:solids ratio as used in the concrete;
- unit weight of concrete;
- compressive strength at 1, 3, 7, 28, 90, and 180 days;
- flexural strength taken at the same times;
- density of hardened concrete at the ages of 1, 3, 7, 28, 90, and 180 days;

- dynamic modulus of elasticity, taken at 1, 3, 7, 28, 90, and 180 days;
- Poisson's ratio taken on selected mixes at various ages;
- chloride ion permeability, as determined by AASHTO T 277-83I "Rapid Determination of the Chloride Permeability of Concrete" [3];
- resistance of concrete to freezing and thawing, as determined by standard ASTM C 666 testing [4]

In addition, a number of determinations of various specialized kinds were made on cement pastes of the same composition as the concretes, and on other fly ash materials.

Although the research presented were conducted with a limited suite of materials, it is felt that these properly represented the range of materials available for highway construction in Indiana.

The most relevant properties of fly ash affecting both the fresh and hardened concrete have been identified. It is presumed that the information developed in this program can be of assistance in solving future problems in connection with the use of fly ash in concrete, and it is hoped that the insight developed may be of assistance in correctly interpreting the cause and nature of any past difficulties.

1.4 Special Cement Chemical Notation

In this report we have employed the special short notation developed by cement chemists to simplify chemical formulas. For clarity and to avoid difficulties in reading the text by those not acquainted with this specialized notation, we provide an explicit statement of the symbols used below.

Oxide	Symbol
Al_2O_3	A
CaO	C
Fe_2O_3	F
H_2O	H
MgO	M
SiO_2	S
SO_3	$\overline{S}$

Using this nomenclature the chemical formulas of basic cement compounds and reaction products can be abbreviated as follows:

Tricalcium silicate	$3CaO \cdot SiO_2$	=	C_3S
Dicalcium silicate	$2CaO \cdot SiO_2$	=	C_2S
Tricalcium aluminate	$3CaO \cdot Al_2O_3$	=	C_3A
Tetracalcium aluminoferrite	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	=	C_4AF
Calcium silicate hydrate gel (indefinite composition)		=	C-S-H

2.0 REVIEW OF THE LITERATURE

2.1 Properties of Fly Ash

A review is provided below of the properties and origins of different types of fly ashes. Special emphasis is given to aspects of variability of chemical and mineral composition as well as to the parameters influencing behavior in concrete

2.1.1 The Origin of Fly Ash

Fly ash is a mostly inorganic by-product of the pulverized coal burned in the furnaces of coal-burning power plants. It occurs in the form of a fine powder, which is removed by means of mechanical collectors or electrostatic precipitators from the stream of combustion gases prior to its discharge into the atmosphere. Electrostatic precipitators capture the finer particles that usually escape mechanical collectors [6].

A typical schematic of a basic power plant coal burning and fly ash collection configuration is shown in Fig. 2.1-1. The coal is first ground (pulverized) to a reasonable fineness, frequently 70 % finer than the No. 200 sieve, i.e. 74 μm. The fine coal is then mixed with hot air and blown into the boiler combustion zone. The high temperature of that zone (in excess of 1500° C [7]) initiates a series of

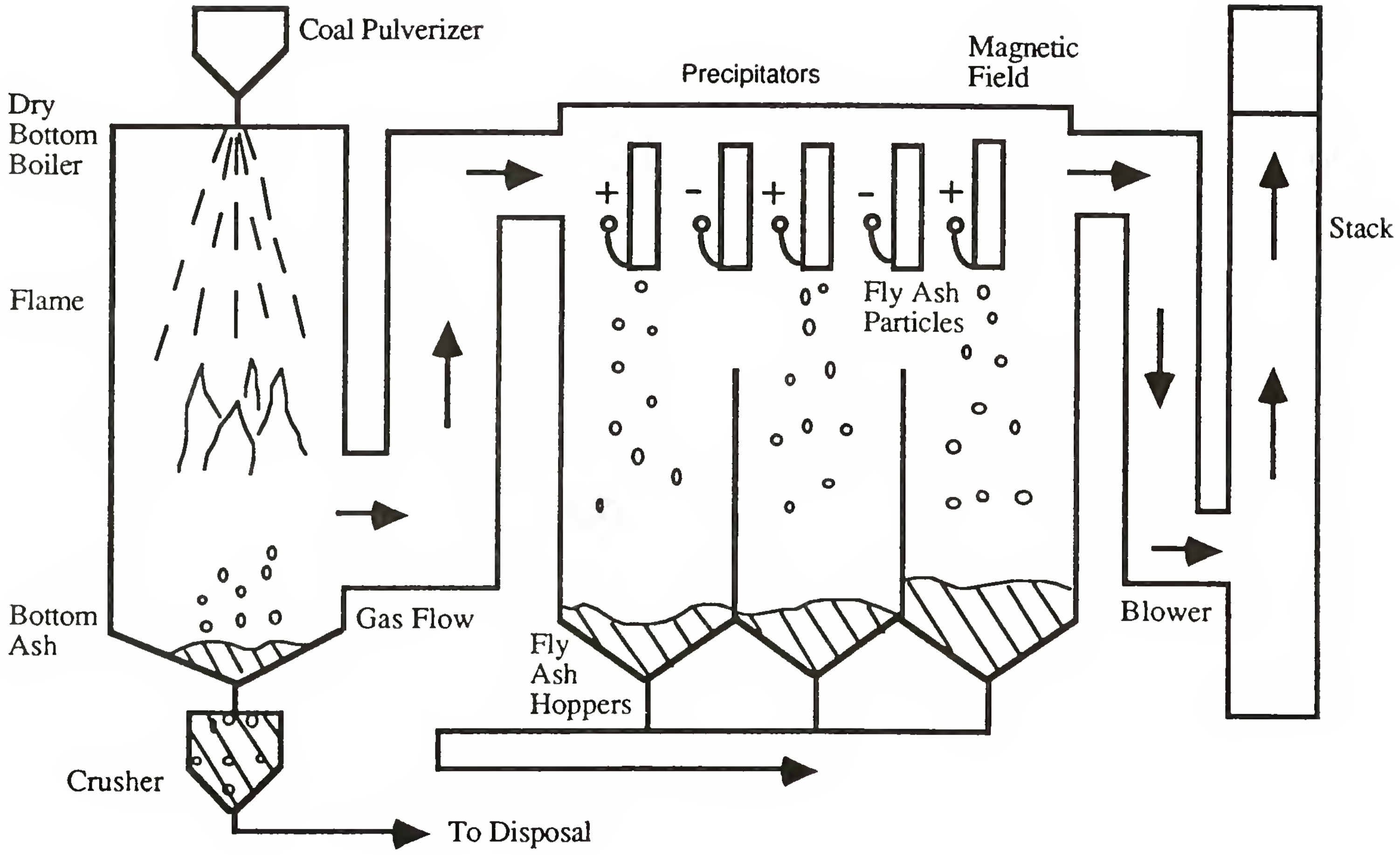

Figure 2.1-1 A typical schematic of pulverized coal combustion and fly ash collection processes [8].

physical and chemical changes in the individual coal particles.

The organic component of the powdered coal is burned off quickly. The grains of mineral inclusion present undergo partial (or complete) melting; the larger grains tend to fuse together [9], especially near the walls of the boiler. The coarser material, containing mostly fused particles deposits as bottom ash, while the finer particles remain in the air stream. Most of the fine particles undergo melting and assume a spherical shape [10]. Those travel out of the burning zone suspended on the gas stream and cool rapidly (1500° C to 200° C in 4 seconds being reported [11]). The cooled fine particle residue is called fly ash. Relatively coarse particles of the fly ash are removed from the air stream in some plants by passage of the air stream through sharp bends designed to decrease velocity; these are called "economizer collection zones" and the so-called economizer ash may be separately disposed of. The remainder of the fly ash is usually collected by several successive banks of electrostatic precipitators from which it is discharged to hoppers, and eventually transported to collection silos or disposal lagoons.

The small droplets of molten material that give rise to spherical fly ash particles may contain quartz grains or rarely other small crystals of inorganic coal components. On cooling, other secondary crystals are precipitated, but usually most of the molten material cools so rapidly that it becomes an inorganic glass, with any crystalline matter buried within the glassy sphere. Residual unburned carbon may be present in some grains.

The chemical composition of each fly ash grain is individually determined by the composition of the inorganic fraction of the coal particle it was derived. Fly ash compositions vary a great deal from grain to grain, but tend to have a stable average composition for the material as a whole. This average composition reflects the overall composition of the inorganic components present in the coal, but it is also affected by the degree of coal pulverization, by the design of the boiler unit and the specifics of its operation, and by the fly ash collection and storage methods. The latter factors impact on the disproportionation of chemical composition between fly ash and bottom ash, on the amount of unburned residual carbon present, and on what proportion of the overall combustion residues are delivered as fly ash.

The composition of inorganic fraction of the coal being burned is by far the most important factor directly influencing the composition of the fly ash [12]. Fly ashes of highly variable composition are of little value for use in concrete due to the unpredictable results they can produce in both fresh and hardened material.

In concrete, fly ash is classified as an artificial pozzolan, i.e. a siliceous or aluminous material in reactive form which, in a finely divided state, is capable of combining with lime in the presence of water to form stable calcium silicates having cementitious properties [13]. In addition to being pozzolanic, some fly ashes contain significant amounts of calcium oxides. As a result, calcium silicate and aluminate hydrates can be formed and those fly ashes display self-cementitious properties analogous to those of portland cement.

As supplied, fly ash may often closely resemble cement in texture and grain size. Depending upon the contents of carbon, iron, etc.

the color of fly ash may vary from light tan to a dark gray.

2.1.2 Classification of Fly Ash

As mentioned previously, the overall chemical composition of a given fly ash is strongly influenced by the composition and properties of the coal it was derived from. Coals ordinarily used in power generating stations are usually classified into three ranks, depending primarily on the content of burnable material and the energy-producing potential. Those groups, in descending order of caloric content are:

- Bituminous coals
- Sub-bituminous coals
- Lignitic coals

The carbon contents of bituminous coals are typically higher than those of the other types, which contain larger percentages of noncombustible materials. In consequence, sub-bituminous and lignitic coals yield larger amounts of "coal ash" (a generic term used to describe both bottom and fly ashes) per ton of coal burned [7].

ASTM Specification C 618 [5] divides fly ash for use in concrete into two groups, Class F and Class C pozzolans. The classification is on the basis of chemical composition, specifically the sum of the contents of silicon, iron, and aluminum oxides. Separate provisions are made for certain chemical and physical requirements to be met for each class.

Class F fly ashes are ordinarily associated with bituminous coals and Class C fly ashes with sub-bituminous and lignitic coals, but the linkage of fly ash class with coal type is in fact not well founded [10].

Table 2.1-1 lists the basic ASTM C 618-85 requirements. Note that Class F pozzolans are required to have the sum of silicon, iron, and aluminum oxides be greater than 75%, and for Class C pozzolans the sum must be greater than 50%. Thus, in logic at least, all Class F pozzolans also meet the Class C compositional requirements. In practice, it also turns out that many fly ashes derived from subbituminous or lignitic coals can meet the Class F requirements [14], and the use of the sum of the oxides as the primary classification parameter has often been criticized.

The content of calcium, expressed by convention as the percentage of CaO, has a major influence on the potential cementitious behavior of the fly ash, but its value is not used in the ASTM classification scheme. Indeed, no analysis for calcium is required in the ASTM classification. Its effect is indirectly accounted for in that a large percentage of CaO necessarily reduces the percentage of the combined aluminum, silicon, and iron oxides.

The common dissatisfaction with the present ASTM C 618 has led to several other proposals for fly ash classification [15-17]. In general, those proposals call for discontinuation of the present practice of fly ash classification based upon its chemical analysis, and recommend defining the type of a fly ash based on its properties and performance in concrete.

Table 2.1-1 Summary of chemical and physical requirements defined in ASTM C 618-85 for fly ashes for use in portland cement concrete.

	Class F	Class C
A. Chemical requirements		
(SiO_2 + Al_2O_3 + Fe_2O_3), min., %	70.0	50.0
SO_3, max., %	5.0	5.0
Moisture content, max., %	3.0	5.0
Loss on ignition, max., %	6.0*	6.0
Optional chemical requirements		
Available alkalies, as Na_2O, max., %	1.50	1.50
B. Physical requirements		
Fineness:		
Amount retained when wet-sieved on No. 325 (45μm) sieve, max., %	34	34
Pozzolanic activity index:		
With portland cement, at 28 days, min., % of control	75	75
With lime, at 7d, min., psi (kPa)	800(5500)	
Water requirement, max., % of control	105	105
Soundness:		
Autoclave expansion or contraction max., %	0.8	0.8
Uniformity:		
Specific gravity, max. variation from average, %**	5	5
Percent retained on No. 325 (45μm) sieve, max. variation, percentage points from average**	5	5

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*Reduced from 12% in 1984, with the provision that Class F pozzolan containing up to 12.0% loss on ignition may be approved by the user if either acceptable performance records or laboratory test results are made available.

**Average established by the ten proceeding tests, or by all the proceeding tests if the number is less than ten.

In practical terms, greater attention should be paid to the mineralogical composition, type and content of glass, and to the analytical content of constituents other than silicon, aluminum and iron oxides, especially, but not limited to, CaO.

The first level distinction among fly ashes is realistically made on the basis of CaO content, with low calcium fly ashes being distinguished from high calcium ashes. There is no agreed-upon boundary level, but 10% CaO seems reasonable, and most engineers knowledgeable in the field would have little difficulty with a boundary of somewhere near this value.

This terminology has been adopted and used when appropriate in the present report.

2.1.3 Structure and Composition of Fly Ashes

Fly ash is an assemblage of particles whose individual diameters may vary from as little as 0.5 μm to well over 100 μm [18,19]. Shape, surface texture, and color are also variable. Most fly ash particles are small solid spheres; some are hollow with thin or thick walls, and with or without smaller particles included in the hollow cavity; some are rounded but have projections; and many large ones are angular agglomerations [10,20]. The grain surfaces are often smooth and glossy, but some fly ashes may show surface deposits and varied surface morphology [10,18].

The overall composition of a fly ash varies with the type and source of coal, grinding fineness, burning procedure, the combustion temperature, and collecting techniques. The chemical components of fly ashes are traditionally reported as oxides, even though they do not appear in that form. The usual analysis includes significant contents of silica (SiO_2), alumina (Al_2O_3), ferric oxide (Fe_2O_3), calcium oxide (CaO), magnesium oxide (MgO), sodium oxide (Na_2O), potassium oxide (K_2O), titanium oxide (TiO_2), and sulfur trioxide (SO_3).

In addition, every fly ash contains some unburned carbon, which is customarily reported as Loss on Ignition (LOI).

From the mineralogical point of view fly ashes consist mostly of glass [10,28,29]. In the low calcium fly ashes the glass is predominantly of aluminosilicate composition and tridymite-like structure; the glasses of high calcium fly ashes incorporate a considerable amount of calcium and a different structural type [30]. A recent investigation [31] has shown that particular high calcium fly ashes may contain a glass of intermediate or lower calcium content along with a substantial content of calcium-bearing crystalline compounds.

Although glass is the predominant mineralogical component in most fly ashes, various crystals may also be present. These are individually present in small amounts (up to a few percent) and most of the time are embedded within the glass; occasionally crystalline surface deposits may be found as well [21].

Many researches [10,20,21,32,33] have determined that the principal crystalline minerals present in low calcium fly ashes are quartz, mullite, hematite and magnetite (ferrite spinel).

Other types of crystalline compounds have been found [20,21,29,34] in the high calcium fly ashes. Those include such components as crystalline CaO (free lime), C_3A, and anhydrite. Some of the high calcium fly ashes contain crystalline MgO (periclase), C_2S and even C_3S. Crystalline alkali sulfates may be present on some fly ashes, often as surface deposits [20].

The reactivity of a fly ash in concrete will vary with its glass type and content and with mineralogical composition, both of which are largely a function of overall chemical composition. Diamond reported in 1981 [10,20] that the primary reactive component in low calcium fly ashes is the glass, with most varieties of the embedded crystals being inert. On the other hand Idorn [35] suggested that many of the crystalline minerals in high calcium fly ashes are reactive.

2.1.4 Physical Properties

Examination of the literature on the characterization of fly ashes for use in concrete reveals that fineness and specific gravity are usual physical properties reported, along with pozzolanic activity index (PAI). The later is not strictly a physical property as such, but it is often classed as one.

Fineness is commonly regarded as an important parameter, especially in its influence on the rate of chemical reactivity, on workability, and on water demand in concrete [36-38]. Virtually every specification dealing with the use of fly ash in concrete (see for example a review of international standards by Rossouw et al. [39]) recognizes the importance of fineness by listing some minimum measure of fineness as one of the mandatory physical requirements.

The parameters used to characterize fly ash fineness include sieve residue, specific surface area, and particle size distribution.

Published opinions differ as to which parameter is most appropriate in terms of correlation with the behavior and properties of fresh and hardened concrete [40-43].

The weight percentage retained on a particular sieve (usually 45 µm) is the simplest and cheapest measure of fineness, although it has serious shortcomings. It yields only a single number, indicative primarily of the percentage of oversized particles. Fly ashes vary considerably in the shapes and details of their particle size distributions curves, and this single figure is a relatively poor indicator of reaction potential. A full particle size distribution is more meaningful, and when adequately presented and interpreted, such a measure can provide important information regarding the potential influence of a given fly ash on concrete [36].

The measurement of fly ash specific surface is another method used to assess its fineness, but the results tend to be variable and are strongly distorted by the presence of unburned coal particles [44-46]. Major discrepancies are observed among values of specific surface obtained for a given material using different methods of measurement [45].

However measured, fineness can serve as an important indicator of the influence a given fly ash will have on the properties of concrete. Finer ashes are generally preferable, as they tend to reduce the amount of water needed for a given slump and they increase the rate of chemical reactivity [23,47-50]. The relationship between fineness and expected reduction in water demand is not universal, and the literature does contain data to the contrary

[46,51-53].

A large number of tests [40,54-60] have been devised for the purpose of assessing the pozzolanic properties ("activity") of fly ashes, but their results are controversial. They tend to correlate poorly with field performance of fly ash concretes, as well as to chemical composition [40,56,57,60,61].

In the present ASTM pozzolanic activity test (ASTM C 311 [54]), the potential reactivity of a fly ash is estimated by measurement of strength development during high temperature reaction with lime or portland cement. The results of such purely physical tests are reported as pozzolanic activity indexes (PAI). The PAI is expressed as the ratio of the average strength of the fly ash-bearing mortar to that of the reference cement mortar.

In most of the existing literature PAI has been found to correlate to some extent with fineness and with surface characteristics of fly ashes, but not with their chemical and mineralogical composition [38,63-65].

The specific gravity of fly ash is significantly less than that of portland cement, and can vary from about 1.6 to about 2.8. Although its value does not seem to have a direct effect on concrete quality, its variation may serve as an important indicator of changes in fly ash characteristics such as fineness, particle morphology, or contents of iron oxide on one hand and carbon on the other. The specific gravity value for a given fly ash is important in mix proportioning, as variations in it change the volume proportions of the mix.

2.1.5 Fly Ash Behavior in Concrete

Fly ash influences the properties of concrete in both its fresh and hardened states. Some of the changes observed are due to chemical reactions taking place over time, but immediate effects on fresh concrete may be produced by physicochemical and physical effects associated with modification of flocculation, particle packing, and influences of these on water demand.

Physical Phenomena:

The physical effects depend on the type and relative amount of fly ash used. As the specific gravity of fly ashes is lower than that of portland cement, one of the prospective results of a weight replacement is an increase in the volume of paste in the concrete which may lead to improved cohesion and plasticity.

The predominantly spherical shape of fly ash particles is commonly believed to contribute to concrete workability by reducing the friction at the aggregate-paste interface and by producing a "ball-bearing" effect at the point of aggregate contact. Although the literature does contains some evidence to support that theory [66,67], such explanations seem to be oversimplified.

Based on more recent studies [68-70] the improved workability, or reduced water requirement, of fly ash bearing concretes has been attributed primarily to the physicochemical effects. According to these theories, the water reduction occurs by a deflocculating effect caused by adsorption of the finest fly ash particles on the surface of cement grains. Kobayashi and Sato [71] reported that by helping to separate and disperse the clusters of cement particles, the presence of fine particles of fly ash increases the rate of early cement hydration. The strength of concretes containing fly ash as fine aggregate replacement was found to be greater than that of the reference concrete as early as at seven days. It is difficult to determine however to what extent such results reflect physical or physicochemical responses rather than more rapid pozzolanic reaction.

The reduction in water demand for a given slump upon fly ash addition is not universal. The effectiveness of a fly ash in that regard depends on many parameters, the most important being particle distribution and content of unburned coal, as reflected in the LOI. Coarse fly ash grains and the presence of unburned carbon tend to increase the amount of water required for a required workability [29].

Chemical Phenomena:

Although the chemical effects associated with the presence of fly ash in concrete have been studied extensively, there is still some lack of understanding of all processes occurring. This lack is mostly owing to the complex nature of the reactions and to the fact that the effects produced may be substantially different, depending on whether low or high calcium fly ashes are used.

The fastest response, taking place within minutes after introduction of water, is the dissolution of any soluble surface deposits present on the fly ash grains. Such deposits, where present, are often alkali sulfates, and their dissolution changes the concentrations of these substances in the mix water and therefore may change the pattern of early hydration [20,72]. The literature contains conflicting reports with regard to the nature of the change, both retardation [18,73-75] and acceleration [76-78] having been reported.

Subsequently the fly ash grains became covered with a "duplex film" composed of layers of calcium hydroxide and C-S-H gel [79,80]. As the cement hydration proceeds, the original duplex film may densify and form shells around the fly ash grains [81,82].

It is generally accepted that the actual reaction of the fly ash particle itself starts when the outer glassy part of its structure comes under attack from the pore solution. There is a considerable lack of agreement as to when this effect occurs. There have been reports of such reaction taking place as early as a few hours after mixing [81] but it is likely that contribution to strength of such reactions is not significant until later ages [83].

In low calcium fly ashes the reactions taking place involve both hydration of the siliceous glass and reaction with alkalies and calcium hydroxide released during cement hydration [21]. A similar pattern is observed with high-calcium fly ashes [84]. The latter, however, contain glass of a different type along with a moderate content of crystalline calcium compounds and therefore tend to be more reactive. Some high calcium fly ashes are actually self setting [21].

In general, the extent and speed of the chemical processes occurring in the cement - fly ash - water mixture depends on the type and the amount of the fly ash used, the mineralogical composition of the fly ash, and the composition of the solution with which it is in contact. The influence of such parameters as the type of cement, the temperature, or admixture additions can also be significant.

2.2 Effects of Fly Ash on the Properties of Concrete

A review of literature related to the influence of fly ash, used as a partial replacement for cement, on the properties of concrete is presented in this section. A broad range of properties is discussed, with particular emphasis on slump and workability, air content, setting time, strength and elastic properties, freeze-thaw resistance and chloride ions permeability. It is important to keep in mind that the results discussed in the literature review were obtained by different investigators, using different cement and fly ash sources.

2.2.1 Properties of Fresh Concrete

The workability of fresh concrete is one of the vital parameters related to its field application, and one that is frequently influenced by incorporating fly ash into the concrete mixture. Workability is a complex rheological concept, closely related to the water needed to produce a given slump, but involving other characteristics as well. Changes in workability accompany changes in water requirements of induced by changing one or more of the ingredients of a concrete mix.

Many fly ashes, when used as a partial replacement for cement, have been shown to reduce the water requirement and to improve the workability of the mix. Kokubu [66] reported the results of tests conducted on twenty different fly ashes marketed in Japan. When used at a replacement level of 25%, those fly ashes produced water reductions ranging from 4 to 11 percent; the average was 7%. Kokubu estimated that a water reduction of about 5% can almost always be expected, providing that the fly ash used is of appropriate fineness [66].

A reduction of about 7% in the amount of water required for a given slump was reported by Compton and MacInnis [49], who used mixes in which 30% of fly ash was substituted for cement. A similar reduction (7.2%) was observed by Pasko and Larson [48], who examined mixes in which 30% of fly ash replaced 20% of cement.

Examining the workability of four concretes of different water: cement ratios, in which fly ash was substituted for cement on an equal volume basis, Brown [50] reported that the reduction in water demand ranged from 3 to 4%. Similar observations were reported by other investigators [23,53,85].

As previously mentioned not all fly ashes will cause a water reduction, and instances of increased water demand (reduced workability) have also been reported [29,46,51-53,86]. The amount of water required is affected by the physical differences among various fly ashes, and also by the mix proportions used. It will vary depending on whether an equal volume or an equal weight substitution of fly ash for cement is used.

The bleeding of concretes containing fly ash may either be increased or decreased, depending on the type of fly ash used, the cement content, and the fines content of the sand. Fly ashes that improve workability also lower the water requirement of the mix, which results in less bleeding. In addition, the presence of fly ash may compensate for the deficiency in content of sand fines in a given mix and break the continuity of bleed water channels [37]. An example of such improvement in harsh mixes that are subject to bleeding was reported by Copeland [87]. The use of fly ash to reduce bleeding of fines deficient concretes was also recommended by Johnson [88]. On the other hand, Carette and Malhotra reported [53] increased bleeding (over that observed for plain concrete mix) for 6 out of 11 fly ashes tested.

Several investigators have studied the effect of fly ash on the air entrainment of concrete. There are many reports [37,48,89-91] of fly ashes that cause an increase in the amount of air entraining agent (AEA) required to produce a given percent of air in the fresh concrete. This phenomenon is usually linked to the presence of unburned carbon particles in the fly ash, as represented by high values of LOI.

As suggested by Lane and Best [37], the content of carbon particles itself may not be the only reason for the increased amount of AEA required with some fly ashes. They pointed out that carbon particles in grains coarser than 45μm tend to be more porous, and therefore large carbon particles have a more adverse effect on the air content.

The influence of the fly ash type (i.e. Class C or Class F) on the amount of AEA needed is also related to the amount of carbon present. As previously mentioned, high calcium fly ashes tend to have a lower LOI and consequently do not tend to increase the required dosage of AEA to the same degree as their low calcium counterparts [92,93].

The apparent interaction between the carbon present in the fly ash and the air entraining admixture has not yet been completely explained. It is commonly believed that carbon can adsorb molecules of AEA [94,95], or alternatively, that it breaks the air void structure stabilized by the air entraining agent [96].

The active role of carbon was confirmed in the experiments carried out by Burns et al. [97]. According to their observations, pre-exposure of fly ash containing carbon to chlorine gas, calcium hypochlorite, or certain surfactants all reduced the demand for AEA. This was interpreted as due to the deactivation of carbon by the adsorption of chemically active species.

In addition to initially higher AEA requirement, problems of air loss with time (i.e. stability of air content) in concretes containing fly ash have been reported. Gebler and Klieger [92] determined the air contents remaining in the mix at 30, 60 and 90 minutes after initial mixing. The results show an increased rate of air loss (lower stability of the air content) in mixes with increased AEA demand.

Similar conclusions have been reached by Meininger [98], who has found that this loss of air depends upon the amount of easily-digested organic material in the fly ash, as determined by a sodium dichromate digestion test. The results of this test correlate much better with the loss of air than do the results of the loss on ignition test.

With regard to the influence of fly ash on the setting time of portland cement concrete, it seems to be generally accepted that low-calcium fly ashes retard setting. Carette and Malhotra [53], analyzing the behavior of eleven fly ashes with CaO content ranging from 1.4 to 13 %, showed that all except one significantly increased both initial and final time of setting. In another study Mailvaganam et al. [99] obtained an increase in the setting time by approximately 1 to 1-3/4 hour when examining the properties of concretes that contained low calcium fly ashes. Two of the low calcium fly ashes used in the study by Diamond and Lopez-Flores [72] showed strong retarding effects, delaying the initial set for about 2 hours and the final set by as much as 8 hours.

The mechanism of the set retardation does not seem to be fully understood. Jawed and Skalny [75] attributed it to the chemisorption of Ca^{2+} on the fly ash surfaces, and subsequent delay in the nucleation of calcium hydroxide from solution. On the other hand Helmuth [100] suggested that this retarding effect might be the result of covering of the cement grains with fine fly ash particles, or alternatively, adsorption of dissolved organic compounds.

Setting time can either be accelerated or retarded in the presence of high calcium fly ashes, which are generally lower in carbon and higher in reactive constituents than low calcium fly ashes. All three of the high calcium (over 30 % CaO) fly ashes tested by Diamond et al. [72] showed severe retardation of the setting time, comparable with the effects of low calcium fly ashes discussed earlier. A retarding effect was also observed by Ramakrishnan et al. [101] who used a fly ash with 20% CaO. However, one of the high-calcium fly ashes examined by Dodson [102] caused a reduction in a setting time, and similar findings were reported by Covey [103].

In addition to the changes produced in normal setting behavior, some high calcium fly ashes may contain substantial amounts of free

CaO which causes false set in concrete mixes.

Replacement of part of the cement with a low calcium fly ash helps to reduce the temperature rise in fresh concrete. In fact, the first major use of such fly ash was in the construction of a gravity dam where it was employed mainly to control temperature rise [104]. Various investigations [105,106] have confirmed this observation for fly ashes from different sources. It is estimated that low calcium fly ash concrete produces only from 15 to 30 % as much early-age heat generation as an equivalent mass of portland cement in concrete [107].

The influence of high calcium fly ashes on the heat evolution rate depends on their reactivity, and tends to parallel the strength development rate [64]. Some of the high calcium fly ashes can react rapidly with water and therefore may generate heat at an excessive rate.

2.2.2 Strength

Existing literature presents conflicting evidence on the effect of fly ash incorporation on concrete strength development. This is partly because of the differences in the mix proportioning methods used, which can mask the effect of a given fly ash. More detailed analysis of this phenomenon is presented subsequently in Section 2.3.

The compressive strength of plain portland cement concrete is primarily a function of age, water:cement ratio, and the richness of the mix, i.e. the cement content per unit volume of concrete. The ability of a fly ash to lower water demand can play an important role in increasing the ultimate strength, if advantage is taken of the reduced water demand. It is difficult, however, to separate this effect from the influence of factors such as chemical composition of fly ash, reactivity, and the temperature and curing conditions. For this reason, in the discussion that follows, a picture of the general trend in strength development of fly ash concretes will be presented, but an attempt will also be made whenever possible to relate variations that occur to the differences in specific fly ash properties.

It is generally acknowledged that the early rate of strength development of fly ash concretes containing low calcium fly ash is lower than that of similar concrete containing cement alone. One has to remember, however, that most of the published data that show significant early strength gain deficiencies were obtained (1) with fly ashes from older power plants that generally produced coarser fly ashes of higher carbon contents, and (2) for concretes proportioned by simple replacement methods (See Section 2.3.1). Over-replacement, i.e. incorporating more fly ash than the amount of cement removed will usually help to obtain the required strength at a given age [108]. Furthermore, while early strengths, up to 3 days, may be somewhat reduced, 28 day compressive strengths of fly ash concretes are usually comparable to those of corresponding plain concretes [37].

The fundamental reason for this is that fly ash contributes to strength mainly through pozzolanic reaction. This requires the presence of calcium hydroxide, a by-product of cement hydration, so it does not occur until a necessary amount of time has elapsed. Consequently, although their early strength gain is lower, fly ash concretes frequently exhibit higher ultimate strength than plain concretes at ages above 90 days [1,37,109-112]. The increase in strength also continues for a much longer time than in plain concretes [122].

The rate of strength development of concretes containing high calcium fly ashes seems to be affected only marginally by the fly ash. The self-cementing ability of these fly ashes allows for achieving a strength level comparable with the strength of ash-free concrete at any age, even as early as one day after mixing [123,124].

The influence of temperature on the strength development of fly ash concretes is also worth noting. While ordinary portland cement concrete cured at temperatures in excess of 30°C tends to have a reduced strength at maturity, concretes containing fly ash show increases in late strength [106,125-127]. On the other hand, the strength gain of fly ash concretes at low temperatures is slow, and in practice such concretes require more attention when placed and cured in cold weather.

2.2.3. Permeability, Carbonation Resistance, and Corrosion Protection.

For ordinary concrete with the usual impermeable aggregate, the permeability of concrete is controlled primarily by the size, distribution, and continuity of the pores within the paste component of the mortar phase. These in turn are influenced by such factors as the content of cementitious material, water:cement ratio, the fine aggregate grading, the air content, the degree of consolidation, the curing effectiveness, and the degree of hydration.

Incorporation of fly ash into the concrete mix favorably changes some of these factors by influencing (usually reducing) the amount of mix water, breaking the bleeding channels, increasing cohesiveness, improving compactability, and (through pozzolanic reactions) reducing the amount of leachable $Ca(OH)_2$ while producing additional contents of calcium silicate hydrate phases. Since these factors tend to increase the tightness of concrete, it would appear that fly ash inclusion should in general help to reduce the permeability.

Existing research data show that the effectiveness of fly ash in this regard depends on the replacement level, age of concrete, and curing history. Manmohan and Mehta [128] observed a significant drop in permeability of cement pastes containing 10, 20 and 30 % of fly ash during curing periods of 28 to 90 days. This is consistent with results of Davis [129] who reported that although at 28 days the permeability of pipe made from fly ash concrete was higher than that made from plain concrete, after 6 months of curing it was substantially lower.

Improved watertightness and reduced permeability of well-cured fly ash concretes have also been reported by other workers [23,105,130,131]. All these data suggest that the permeability of fly ash concrete at a given time is inversely related to the quantity of hydrated material and decreases along with the progress of pozzolanic reaction.

The permeability of concrete, along with the amount of calcium hydroxide and the degree of water saturation, will influence the rate of reaction of cement hydrates with atmospheric carbon dioxide - a process known as carbonation. Carbonation reduces the alkalinity of the pore water in cement paste and therefore reduces the protection of the steel with respect to corrosion.

The effect of fly ash on the rate of carbonation of concrete is not clearly understood, primarily because of the differences in the mix proportioning and testing methods employed. In 1980 Massazza [132] suggested that the rate of concrete carbonation should be linked to the permeability of the paste in it. Essentially the same idea was proposed as early as 1968 by Smolczyk [133] and was based on the results of five-year carbonation studies carried out by three German laboratories.

The more recent research data seem to confirm that theory. It was shown [134-136] that if the amount of mix water is not reduced to take advantage of the reduction in water demand produced by adding fly ash, when even good quality fly ash replaces a part of the cement, lower early strength and increased permeability could be expected, thus leading to more rapid carbonation of the surface region.

However, when full advantage is taken of the water-reducing capabilities of a fly ash, the resulting concrete will have a lower water:cement ratio (for the same workability) and a tighter structure. This will, in turn, reduce permeability and slow the carbonation rate. The validity of such reasoning was recently confirmed by Lewandowski [137] who found the rate of carbonation of properly designed fly ash concrete to be comparable with the rate exhibited by a reference plain concrete.

There is a growing body of opinion which links the rate of carbonation to the compressive strength of material. Based on his recent studies, Schubert [138] concluded that no significant difference in the carbonation rate exists between concretes and mortars with and without fly ash, as long as they have the same compressive strength and were produced using cement with normal CaO content. Similar conclusions were reached by other researchers [139-144].

Since reduction in the amount of mix water used will bring about strength increase, both of the above theories regarding the influence of fly ash on the rate of carbonation of concrete point in the same general direction. If two concretes, one with and one without fly ash, are designed for equal workability or equal strength, they may be expected to carbonate to a similar degree. In other words, it appears that good-quality fly ash concrete will be comparable to similar plain portland cement concrete in its resistance to carbonation.

Another concern frequently raised with regard to the use of fly ash in concrete structures is the supposed loss of alkalinity of the pore solution and suspicion that this might lead to corrosion of the reinforcing steel.

In general a good quality, well-compacted, low permeability concrete provides adequate corrosion protection for reinforcing steel. The highly alkaline pore solution present within ordinary concrete (pH of about 13.5 to 13.8) causes a passivating oxide film to form on the surface of the steel. This protective film is stable in the alkaline environment provided by the hydrated cement paste, and ordinarily prevents the occurrence of the anodic and the cathodic processes associated with the corrosion phenomenon.

The alkalinity of concrete was once thought to be mostly provided by the $Ca(OH)_2$ released during the cement hydration. Since in the course of pozzolanic reaction the fly ash combines with $Ca(OH)_2$ some concerns were raised [29] that incorporation of fly ash could cause a significant reduction in the alkalinity within a concrete, thus increasing the danger of steel corrosion. However, the alkalinity within concrete is actually due to the presence of high concentrations of alkali (K and Na) hydroxides, not dissolved calcium hydroxide, and almost no dissolved calcium is actually present in concrete solutions. Studies by Diamond [145] revealed that pore solutions in mature portland cement/fly ash paste systems also contain very little calcium, and that the fly ash influence on the alkalinity of pore solution was minor. This would indicate that the effect of fly ash is ordinarily too small to substantially affect the maintenance of the passivation layer present on the reinforcing steel.

This conclusion seems to be generally supported by reported research data which has shown that fly ash concrete does not decrease the corrosion protection of the embedded steel when compared with normal concrete of equal 28-day strengths [51,146,147]. In fact a study by Larsen et al. [148,149] has shown that in practice, corrosion protection is increased by the inclusion of fly ash in concrete.

In conclusion, it appears that properly designed and manufactured fly ash concretes will have lower permeability, and should have increased resistance to carbonation and reduced danger of steel corrosion.

2.2.4 Freeze - Thaw Resistance

The freeze-thaw resistance of plain portland cement concretes and of fly ash concretes of similar strength and air content are essentially the same. This has been proven by a number of studies [53,90,101,123,146,147] carried out on concretes containing both low and high calcium fly ashes.

Since control of the air content of concrete is essential to maintain an adequate level of freezing and thawing protection, most research concerning frost resistance of fly ash concretes centers on the variable air-entraining agent requirements induced by fly ashes, and the stability of air content during mixing and placing operations. This problem was extensively reviewed in section 2.2.1, and the results presented tend to indicate that if fly ash is used in concrete, it may be necessary to use a higher dosage of air entraining agent and exercise a greater control over the possible air loss in order to achieve the desired end result.

In general, the resistance to freezing and thawing of fly ash concrete is influenced by all the factors operating on plain concrete, but is also related to variations in properties of the fly ash itself, and to the changes in concrete properties caused by fly ash addition. Because of this, the traditional protective measures against frost action in concrete, such as incorporation of a desirable air void system by air entrainment, are also necessary in concretes containing fly ash. If these measures are properly implemented, concrete with fly ash is produced whose resistance is the same as the resistance of similar plain concrete.

2.2.5 Chemical Resistance

Among the main causes of concrete deterioration by chemical attack are such processes as leaching of calcium hydroxide, acidic dissolution of cementitious hydrates, the action of atmospheric and dissolved carbon dioxide, alkali-aggregate reactions, and the reactivity of cement components with a variety of aggressive agents. Substitution of fly ash for part of cement can either entirely eliminate the occurrence of such processes or greatly reduce their intensity, therefore limiting any adverse impact on the performance of concrete.

The effectiveness of fly ash in this regard can be linked to two types of factors. The first type correlates strictly with the effect of fly ash on the physical properties of concrete, primarily water demand, workability, permeability and uniformity of the matrix. The second type has to do with the resistance of the binder itself, and with the chemical changes created in the system by the chemical composition of the fly ash and the progress of pozzolanic reaction.

One of the most important aspects of the behavior of fly ash concrete in a chemically aggressive environment is its resistance to sulfate attack. Low calcium fly ash derived from bituminous coal is generally considered to increase the sulfate resistance of concrete [12,85,105,150-152]. This beneficial effect is thought to be mostly provided by the straightforward dilution of C_3A content in proportion to the amount of portland cement replaced by fly ash, supplemented by pozzolanic reaction (which will reduce the amount of $Ca(OH)_2$ in the system), and by reduced permeability of the concrete matrix (restricted ingress of sulfate ions into concrete).

The subject of sulfate resistance of concretes made with high calcium fly ashes remains controversial. Based on his experiments performed on a total of 13 concrete mixes made using fly ashes from lignite or subbituminous coals Dunstan [152] reported that few ashes drastically reduced the sulfate resistance. The same author suggested [153] that a good indication of a fly ash resistance to sulfate attack can be obtained applying the concept of a so-called resistance factor "R". The R value is calculated from the results of chemical analysis of the fly ash as $(\%CaO - 5)/\%Fe_2O_3$. Dunstan's data showed that use of fly ash with an R factor less than 0.75 yielded greatly improved sulfate resistance, but that if the R factor was greater than 3, the sulfate resistance was reduced.

In his most recent paper [154] Dunstan reviewed this concept in the light of results from tests carried out over the last 12 years. His analysis of the data indicated that the R value remains a good indicator of a potential sulfate resistance of concretes containing fly ash.

Klieger and Gebler [155] similarly reported that low calcium (Class F) fly ashes significantly improved the sulfate resistance of concretes made with a cement containing 8% of C_3A. Similar concretes made with high calcium (Class C) fly ashes did not perform as well, although their resistance was better than that of the reference plain concrete. For all of these concretes, an excellent correlation was found between the R value of the fly ash used and expansion in the sulfate exposure test.

For concretes made with cements containing lower C_3A contents

(6% and 4%, respectively), these authors indicated that low calcium fly ashes improved sulfate resistance only marginally. Concretes made with high calcium fly ashes exhibited poorer performances in the sulfate environment, and for one fly ash, the sulfate resistance was reduced compared with the control concrete. The correlation between R value and expansion was poor for the concretes made with these lower C_3A content cements, indicating that factors other than those accounted for in calculating the R value may be important in controlling their sulfate resistance.

Similar conclusions were reached by Hartmann and Mangotich [156] who indicated that application of the R value concept can lead to some problems under certain conditions. In particular the method has failed to predict the durability improvement brought about by some high calcium fly ashes, and it was not able to account for the fact that some fly ashes which exhibited high R values actually performed better than ones with lower R values.

In a related publication Wong and Poole [157] reported on the sulfate resistance of mortars obtained during the development of ASTM C 1012 "Standard Test Method for Length Change of Hydraulic-Cement Mortars Exposed to a Mixed Sodium and Magnesium Sulfate Solution" [158]. A total of eleven fly ashes (eight Class F and two Class C) ashes were used in the program. The authors concluded that "there appears to be no strong evidence to support a general hypothesis that Class C fly ashes cause poorer resistance of portland cement systems to sulfate attack".

In summary, the results of the reported investigations show that the influence of fly ash on the sulfate resistance of concrete is not completely understood. Although there is enough evidence that some fly ashes can effectively improve resistance of concrete in sulfate environments nevertheless in severe exposure conditions the use of some high calcium fly ashes may not be advisable.

Another important aspect of concrete chemical durability is its resistance to expansion and cracking resulting from an internal reactions between its alkaline solution and certain reactive constituents present in some aggregates. These are mostly siliceous components. The general phenomenon is known as alkali-aggregate reaction, of which the form known as alkali-silica reaction is by far the most common.

Research data indicate that replacing a part of cement with fly ash can reduce or eliminate the expansion developed [159-162].

The extent to which the addition of fly ash can control these processes in a given concrete depends not only on the type and amount of the fly ash used, but also on such factors as the properties of the reactive aggregate, the specific cement, the mix proportions, the particle size of the susceptible aggregate component, the relative humidity, and the temperature [46,66,159,162,163]. Thus sometimes fly ashes proven to be effective in preventing or reducing alkali-silica reactions when used in particular cement-aggregate mixtures, may be ineffective when combined at different proportions or with a different set of materials.

Research over many years has confirmed that low calcium fly ashes are effective in controlling the alkali aggregate reaction and reducing expansion when used at replacement levels around 25% to 30%. However even that high a content of fly ash is not universally effective, and a replacement level as high as 50% may be required, depending upon the type of aggregate and the alkali content of the portland cement.

Although the amount of data related to the use of high calcium fly ashes in controlling the alkali-aggregate reaction is limited, there are some indications that required replacement levels may be higher than for low calcium ashes [163]. Also, some high calcium fly ashes may contain substantial amounts of soluble alkali sulfates which have been shown to adversely affect the alkali-silica reactivity [29].

The details of the process by which a fly ash is able to control the expansion caused by the alkali-aggregate reaction are still not fully understood. One of the most obvious reasons seem to be the straightforward dilution of the alkali concentration in the pore solution. Pore solution alkalis are mostly derived from the cement, and replacing part of cement with fly ash necessarily reduces the amount of cement-derived alkali available for dissolution. Another proposed mechanism relates to the ability of the highly reactive glass portion of fly ash particles to react with the alkali from the solution more quickly than the reactive aggregate can. This process presumably produces a non-expansive calcium-alkali-silica gel, and reduces the amount of alkalis available for reaction with silica in the aggregate.

The alkali-carbonate reaction is an another variety of alkali-aggregate reaction involving certain dolomitic aggregate components as the reactive rock. The process can damage concrete by causing an expansion similar to that resulting from alkali-silica reaction. In this case however, fly ash seems to be of little help [164].

2.2.6 Modulus of Elasticity, Creep and Drying Shrinkage

Although strength is probably the most fundamental mechanical property of concrete, and as such it is almost always specified for construction projects, it is clearly not the only important concrete mechanical property. In certain applications parameters related to volumetric changes and deformational characteristics of concrete became equally critical with regard to the overall performance of a given concrete structure. These include such properties as modulus of elasticity, creep, and drying shrinkage.

For fly ash concrete the relationship between the modulus of elasticity and age is similar to that of compressive strength and age as discussed in Section 2.2.2. If not designed for equal compressive strength at all ages, fly ash concretes develop their modulus of elasticity somewhat more slowly than do equivalent plain concretes [1,23,37,130]. However when comparisons are made on the basis of equal compressive strength, the modulus of elasticity of fly ash concrete is generally equivalent to that of the reference concrete [64,165,166]. In other words for such cases the type and quality of fly ash does not appear to have a significant effect on the modulus of elasticity values.

In all of the cases reported, the modulus of elasticity increased with age, paralleling the development of the compressive strength. Should the usage of a given fly ash result in additional strength increase at later ages (due to pozzolanic reaction), one might expect a similar development in its modulus of elasticity. This may have important practical implications, as it may beneficially influence the long-term ductility and deflection characteristics of structures under load.

Although published data on creep of fly ash concretes are limited, there seems to be a general agreement among the investigators that for a given 28-day strength, fly ash concretes will exhibit lower creep than equivalent portland cement concretes [37,38,106,165]. This is generally attributed to the fact that after the loading is applied fly ash concretes will have greater subsequent strength gain with time, and therefore exhibit lower creep strains, than corresponding plain concretes.

Based on more recent studies Dhir et al. [166] related the reduction in creep of fly ash concretes to the lower amounts of water these mixes require for a given level of workability. Testing lean mass concrete, Gifford and Ward [167] concluded that fly ash contributes to the creep reduction by increasing the modulus of elasticity, and also by reducing the volume of paste available for creep. The former effect stems from the notion that at early ages part of a slowly reacting fly ash acts as an inert fine aggregate, rather than as a cementitious material.

The results discussed above were mostly obtained for concretes in which the replacement level was below 25%. Studies by Yuan and Cook [168] showed that concretes containing 30% to 50% of fly ash exhibit more creep than the reference plain concretes, or than fly ash concrete with only 20% fly ash.

Drying shrinkage of concrete is another important parameter influencing practical behavior. Most of the research data available on drying shrinkage seems to indicate that the replacement of cement by fly ash has little, if any, influence on this property of the concrete [38,104,168-170]. This general observation holds even in the situations where the replacement of part of the cement with the fly ash results in a larger volume of paste per cubic yard of concrete, thus theoretically increasing shrinkage susceptibility of the concrete.

Among the most common explanations offered in this regard are the reduction in the concrete water demand produced by fly ash and the more restricted loss of pore water associated with the finer paste pore structure developed in fly ash concrete. The type of fly ash does not seem to have any significant effect [53].

2.3 Mix Proportioning Methods for Fly Ash Concrete

This portion of the review chapter is more detailed than the previous portions, since in addition to establishing the background of the field, it also served as the specific basis of a new approach to mix design that is a major feature of the research being carried out. This research was aimed at developing a more rational mix design procedure capable of taking into account the variability of the properties of different fly ashes, and the fact that fly ashes of different origins may have significantly different behavior in concrete. Such an approach is not entirely new in that many investigators have worked on rational method of fly ash concrete mix design for over 20 years.

Actually, the first examples of fly ash concrete mix design were included in the literature 50 years ago [1].

Even a cursory review of the literature reveals the controversy which exists today concerning the role of fly ash in concrete. Fly ash has been viewed as an admixture, as a partial replacement for portland cement and, in a few instances, as a partial replacement for sand. These different viewpoints have resulted in different mix design methods.

In a recent review by Munday, Ong and Dhir [171] those methods have been conveniently classified into three categories:

a) simple replacement methods
b) modified replacement methods
c) rational methods

This classification will be followed in the present review as it not only reflects the chronology of the development of fly ash concrete mix proportioning methods, but also provides for better assessment of differences between various approaches used. Each of those three categories of fly ash concrete mix design methods are reviewed below, and their advantages and drawbacks pointed out whenever possible.

2.3.1 Simple Replacement Methods

The first commercial applications of fly ash in concrete were in massive structures, and the simple replacement method (SRM) was chronologically the first mix design procedure used to proportion concrete mixes for these applications. It is important to remember that at this time the only type of the fly ash available was low calcium fly ash which, by itself, exhibited little in the way of cementitious properties.

Well known examples of early applications using simple replacement mix design methods include several instances of direct replacement of such fly ash for a part of cement in mass concrete in the construction of dams all over the world [104,172,173]. In these early applications, the fly ash concrete mix design was done on an absolute volume basis, and no changes to aggregate quantities were made.

In general, SRM mix design procedure is based on a reference conventional portland cement mix which would be expected to produce the desired strength and consistency (slump). This mix is then modified by replacing a fixed amount of cement by an equivalent amount of fly ash on an absolute volume basis. In order to make sense out of the existing water:cement ratio (w/c) requirements of specifications, the concept of water:(cement + fly ash) ratio (w/c+fa) , or more generally, water:(cement + pozzolan) ratio (w/c+p) was adopted. This is expressed in Figure 2.3-1

ABSOLUTE VOLUME EQUIVALENCY

$$\frac{W}{C + P} = \frac{3.15 \left(\frac{W}{C}\right)}{3.15 \; (1 - F_v) + G_p \; (F_v)}$$

Figure 2.3-1. Expression for water:(cement + fly ash) ratio by volume equivalency [174], (W = weight of water, C = weight of cement, P = weight of fly ash, F_V = fly ash percentage by volume, expressed as a decimal factor, G_p = specific gravity of the fly ash).

As can be seen, a w/(c+p) ratio by weight is calculated in which the absolute volume of (c+p) remains the same as that of the original cement. This will reduce the total weight of cementitious materials, since the specific gravities of fly ashes are normally less than those of cements. As a consequence, this mix design did not give a concrete of strength equivalent to the strength of the plain portland cement concrete, especially at early ages. When less than 30 percent of the cement was replaced, at later ages (generally after 28 days of curing) the fly ash concretes showed greater strength than the plain concretes [46,119,121,175-177]. The general form of strength development curves in plain and fly ash concretes designed this way is shown in two separate illustrations as Figure 2.3-2 and Figure 2.3-3.

High replacement levels of cement (more than 30%) with low calcium fly ash on an absolute volume basis usually leads to significant strength reductions, even at later ages. An example of this is shown in Figure 2.3-4

The water:cement ratio of the mixes used here was 0.5 and 45% of fly ash by absolute volume was used to replace the cement. Even after ten years the compressive strength of the fly ash concrete did not approach that of the portland cement mixture [178].

Strength-gain related difficulties experienced in fly ash concretes designed by the absolute volume replacement methods prompted the development of another version of SRM - this time based on a weight basis. In this method a conventional portland cement mix is adjusted by replacing the fixed weight of cement by the equivalent weight of fly ash. The difference between the specific gravity of the cement

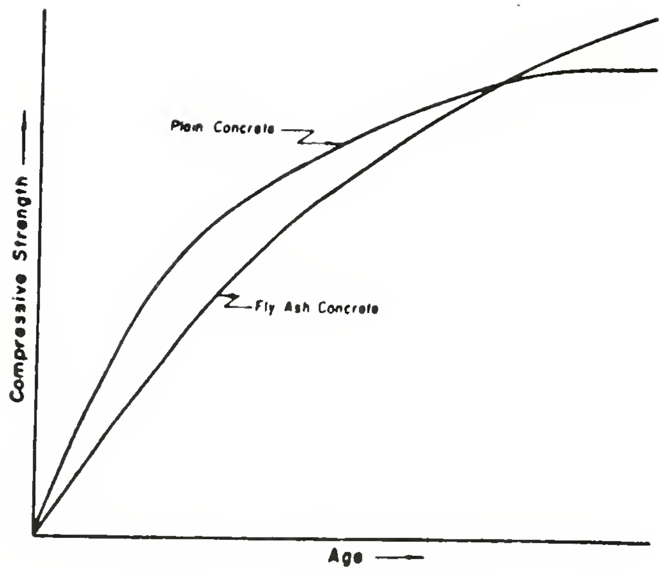

Figure 2.3-2 Rates of strength increase of plain cement concrete and fly ash concrete based on partial replacement of cement [176].

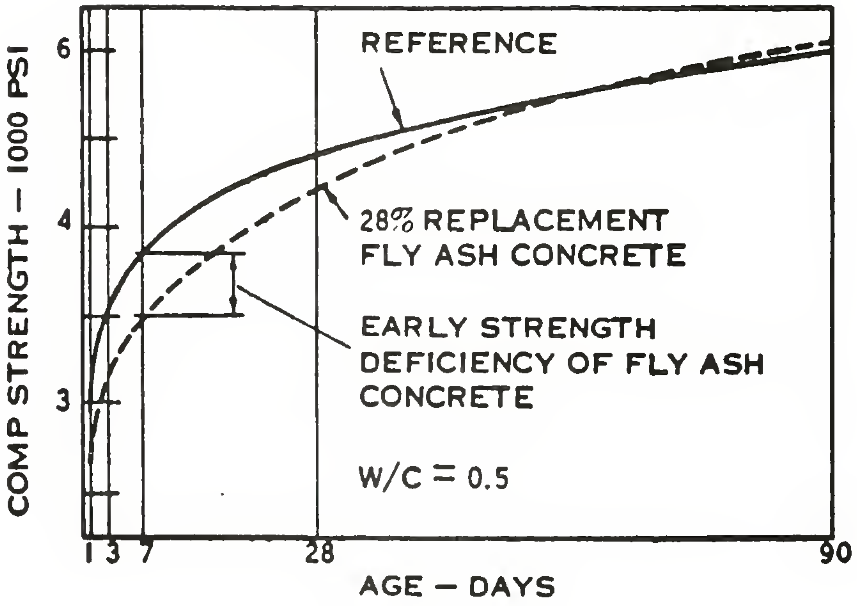

Figure 2.3-3. Strength development of concrete made with and without fly ash based on partial replacement of cement [177].

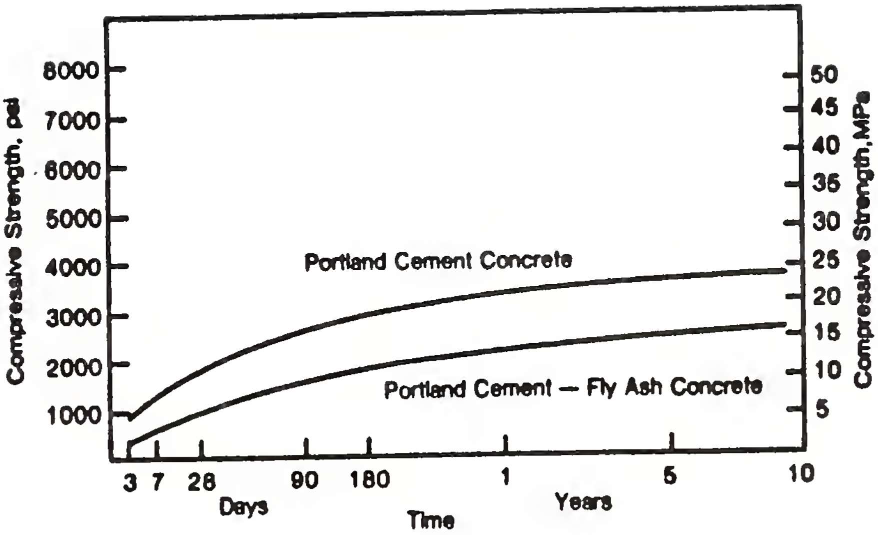

Figure 2.3-4. Compressive strength development for fly ash and plain concretes (water:cement ratio 0.5 and 45% replacement by absolute volume) [178].

and that of the fly ash is disregarded and therefore w/(c+p) = w/c numerically as illustrated in Figure 2.3-5.

WEIGHT EQUIVALENCY

$$\frac{W}{C + P} = \frac{W}{C}$$

$\frac{W}{C + P}$ = WEIGHT OF WATER DIVIDED BY WEIGHT OF CEMENT AND POZZOLAN

$\frac{W}{C}$ = TARGET WATER—CEMENT RATIO BY WEIGHT

Figure 2.3-5. Expression for water-cement and water-cement plus fly ash ratio [174].

Here the fly ash percentage is expressed as a percent of the total weight of cementitious material, as shown in Figure 2.3-6.

% POZZOLAN EXPRESSED BY WEIGHT

$$F_W = \frac{P}{C + P}$$

F_W = POZZOLAN PERCENTAGE BY WEIGHT, EXPRESSED AS A DECIMAL FACTOR

P = WEIGHT OF POZZOLANIC MATERIAL

C = WEIGHT OF CEMENT

Figure 2.3-6. Expression for percent of fly ash by weight [174].

Since the specific gravity of fly ash is lower than the specific gravity of cement, the total absolute volume of cement and fly ash will be slightly higher than the absolute volume of the original cement. In this method the increased volume (or yield) is compensated for by reduction in the volume of aggregate used.

The set of equations shown in Figure 2.3-7 can be used to convert the percent of fly ash by weight to percent of fly ash by volume and vice versa.

WEIGHT AND VOLUME CONVERSION

$$F_v = \frac{1}{1 + \left(\frac{G_p}{3.15}\right)\left(\frac{1}{F_w} - 1\right)}$$

OR

$$F_w = \frac{1}{1 + \left(\frac{3.15}{G_p}\right)\left(\frac{1}{F_v} - 1\right)}$$

F_v = POZZOLAN PERCENTAGE BY VOLUME, EXPRESSED AS A DECIMAL FACTOR

F_w = POZZOLAN PERCENTAGE BY WEIGHT, EXPRESSED AS A DECIMAL FACTOR

G_p = SPECIFIC GRAVITY OF THE POZZOLAN

Figure 2.3-7. Expressions for converting percent of fly ash by weight or volume [174].

In most of the cases reported the weight replacement procedure, when used with low calcium fly ashes, gave higher early strength gains, although still not as high as those of plain cement mixes [96]. As reported by Swamy et al. [179,180], this problem can be eliminated by addition to the mix of either plasticizing/water-reducing admixtures, or superplasticizers. Fly ash concretes with one-day strengths comparable to those of similar reference concretes were produced using these admixtures while replacing 30 percent of cement by weight with low-calcium fly ash [180].

The simple replacement methods of mix proportioning seem to work better with high calcium fly ashes than with low calcium fly ashes. The former usually exhibit some cementitious (self-hardening) capabilities. Thus reaction of high calcium fly ashes in concrete is not as dependent on prior cement reaction; they are able to contribute to the strength gain at early ages.

As an example, the data presented in Figure 2.3-8 show the comparative strength gain rates of concrete in which 20 percent of cement was replaced pound-for-pound with high-calcium (over 10 percent CaO) fly ash. It can be seen that strengths values were increased at every age.

Similarly, Raba and co-workers [124] found, using various replacement values, that fly ash concrete can be designed to achieve the desired compressive strength at either early or late stages utilizing subbituminous high calcium fly ashes.

A successful application of high calcium fly ash using the simple replacement method of mix proportioning for the production of high-strength concrete was reported by Cook [181]. The amount of cement replaced was 20% and 30% on a pound-for-pound basis. All of the mixes tested met the target value for 28-day compressive strength, and significant increases in strength were observed at later test ages (56 and 180 days). To take advantage of this fact, the author recommended that the specification acceptance criteria be modified to extend the test age to either 56 or 90 days. In order to assure proper and

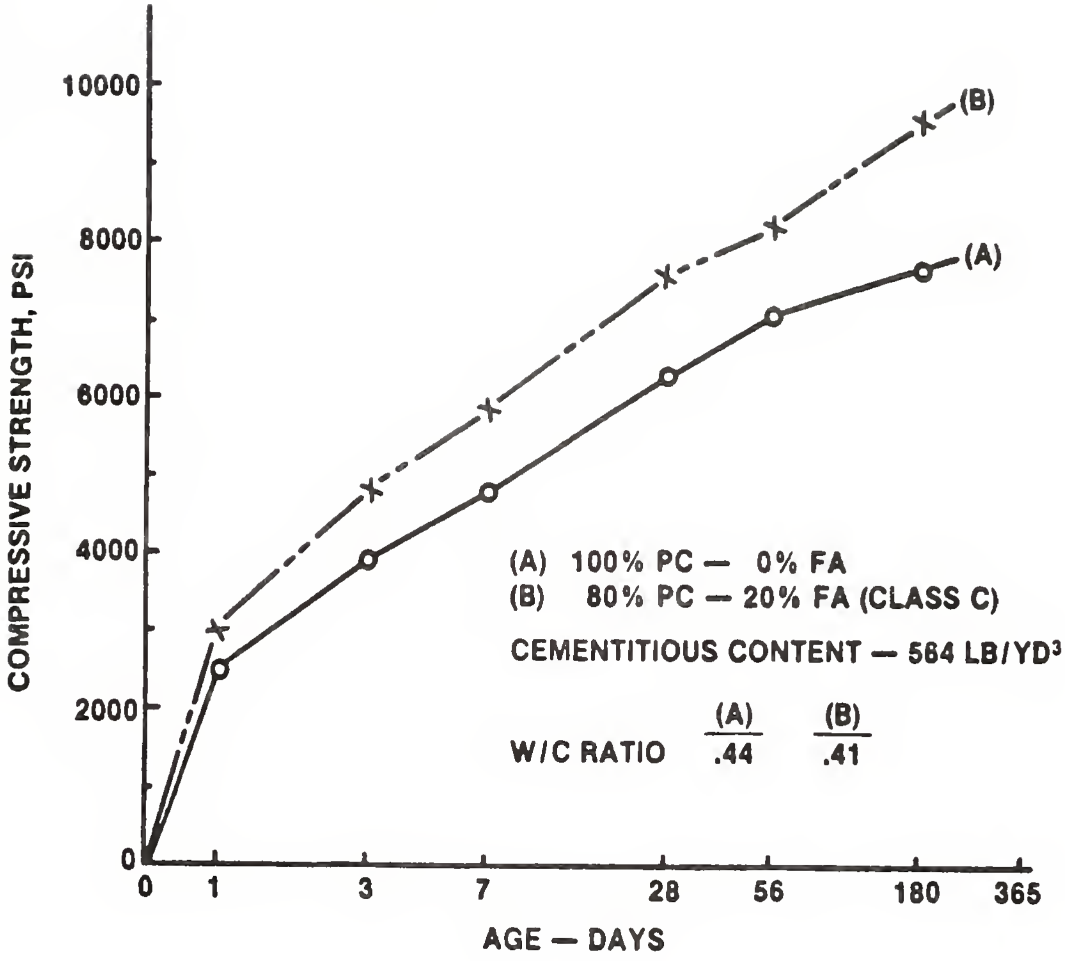

Figure 2.3-8. Comparison of strength gains of plain portland cement concrete and concrete in which part of the cement is replaced by a high-calcium fly ash on weight basis [12].

economical proportioning of fly ash concrete using this method, an optimum amount of fly ash has to be established for a given set of project specifications' requirements. A laboratory trial batch program is recommended for this purpose [12], [181].

The obvious advantage of the simple replacement methods of mix proportioning is their straightforwardness, in the sense that the set of equations which describes the quantitative relationships between individual ingredients is the same as for the plain concrete. These basic relations have been in use for over 100 years, and are well known to concrete producers. When the direct partial replacement of cement by weight is used, the volume of cement paste increases due to the lower specific gravity of the fly ash, and the rheological characteristics of concrete are ordinarily enhanced, providing that the fly ash by itself does not increase water demand of the mix. Data on workability studies reported by Banfill [182] and Cabrera et al. [183] have shown that improvement in flow properties occurs in concretes with both low and high cement contents. The predominant effect of fly ash in improving workability is exhibited as a reduction in the yield value of the mix, without any significant effects on its plastic viscosity. With lower water demand fly ashes, this should allow concrete production at lower processing costs. This is in addition to the lower materials cost associated with the use of a fly ash.

The main drawback of these methods is the fact that they do not take into account the significant variations of the characteristics of different fly ashes. Depending on the nature of the fly ash, its water demand, and the replacement percentage used, the variability of concretes designed by these methods may be quite large. Furthermore, when early strength gain is of concern these methods are not appropriate for use with low calcium fly ashes.

2.3.2 Modified Replacement Methods

All of these methods were developed in response to the need for a mix design procedure which could increase the slow strength gain at early ages of fly ash concretes. Slow early strength gain of concrete is not normally acceptable in regular structural applications.

Modified replacement methods (MRMs) of mix proportioning require that the weight of fly ash put into the mix be greater than the weight of cement removed, usually with accompanying adjustment made in the fine aggregate content. For this reason the extra fly ash introduced into the mix has often been referred to as "sand replacement" fly ash as opposed to "cement replacement" fly ash. Similarly to the SRMs discussed earlier, the MRMs were originally used in conjunction with low calcium fly ashes only.

Probably the first method of this group was developed in 1958 by Lovewell and Washa [108]. Their work indicated that it is possible to produce fly ash concrete of early age (between 3 and 28 days) strengths that are comparable with those of plain concrete, providing that the actual quantity of fly ash used is in excess of the amount of cement removed. In their method the amount of fly ash needed to replace each pound of cement removed was dependent on the cement content of the plain concrete mix, and increased as the cement content decreased. These authors claimed that with relatively few tests a designer could develop data which would allow him to proportion concrete containing fly ash with predictable results.

This concept was further elaborated by Cannon [112] who proposed a procedure for proportioning fly ash mixes to obtain strengths equal to those of reference plain concretes, but at 28 and 90 days. This procedure evolved from the extensive laboratory investigations and field experience of the Tennessee Valley Authority (TVA), and is supplemented by set of graphs which can be used to proportion fly ash concrete mixes for both strength and economy. An example of such a graph is shown in Figure 2.3-9.

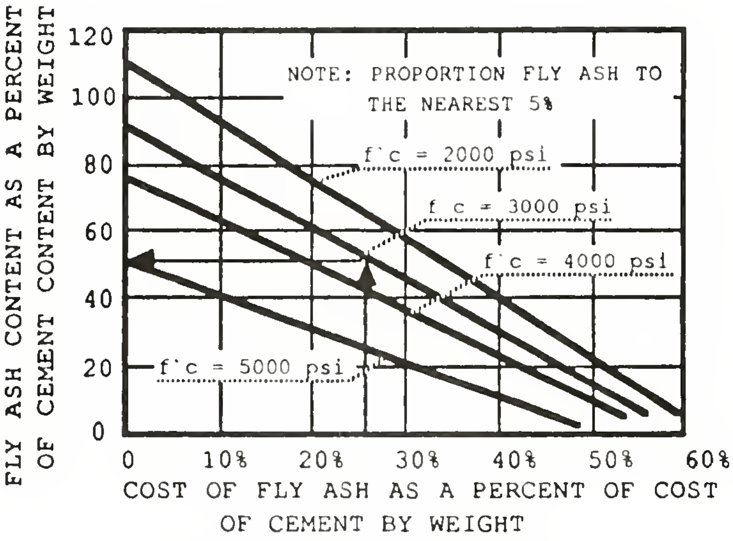

Figure 2.3-9 Economic proportions of fly ash for 28-day strength concrete [112].

This graph allows one to select the amount of fly ash to be used in a mix using criteria based on the relative cost of fly ash compared to that of cement, and on the required ultimate strength of the concrete. For example, if the cost of fly ash is about 25% of the cost of cement, and if 3000 psi concrete is required, the method results in a mix designed for maximum economy that contains about 50% of fly ash and about 50% of cement by weight.

Cannon's approach, like that of Lovewell and Washa [108], results in the use of a higher combined weight of cement and fly ash than the weight of cement in the reference plain concrete mix. The method addresses the fact that, for a given set of materials, the water requirement of the mix will depend on the relative amounts of fly ash and cement. This is illustrated in Fig. 2.3-10, which shows a comparison of water requirements for equal strength concrete in terms of the proportions of fly ash to cement used and the water:cement ratio of the reference mixes.

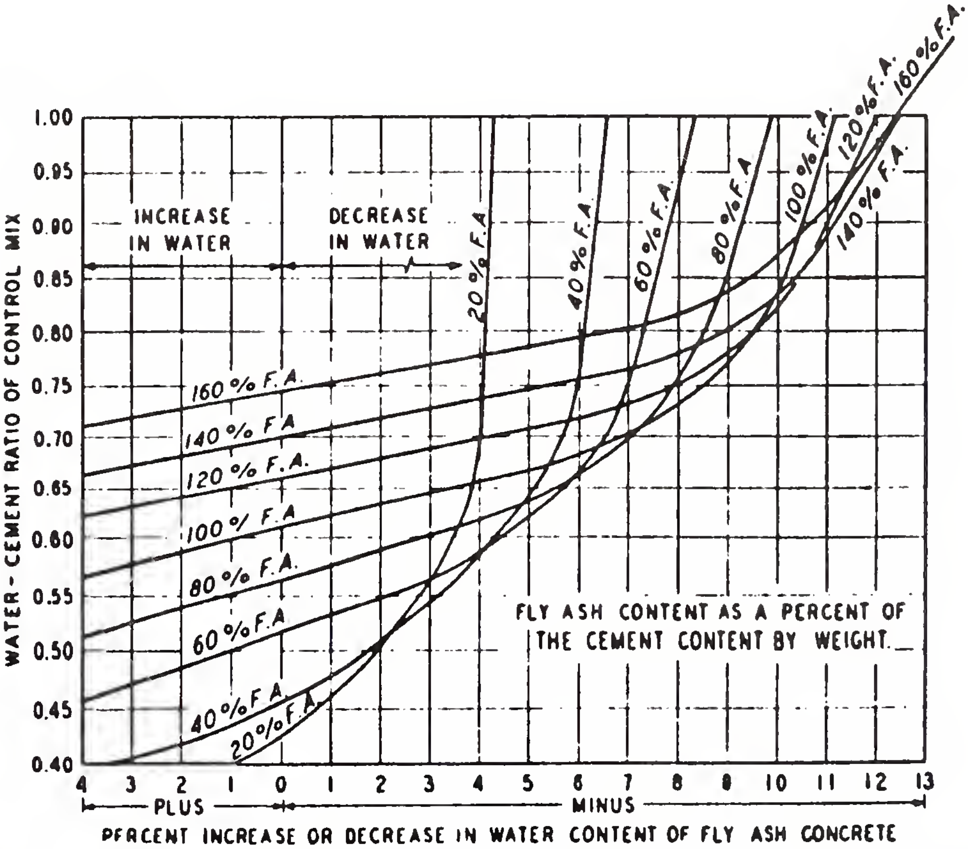

Figure 2.3-10 Comparison of water requirements of concrete with and without fly ash proportioned for equal 28-days strength, identical slump, and air content [112].

This author acknowledges that different fly ashes may differ in water requirement, and that a given fly ash does not produce the same water reduction with all cements. The heavy dependence on the relationships established for one particular set of materials used by Cannon is the major drawback of his method, and prevents its reliable use with fly ashes from different sources.

Cannon's method was further developed and simplified by Ghosh [184] who suggested modifying the basic Abrams' Low relationship between strength and water:cement ratio to take into account the use of a fly ash. Based on the extensive laboratory test results, Ghosh published a series of graphs depicting the relationship between the cement content of the plain concrete mix and the cement plus fly ash content of fly ash concrete mixes for strength at a given age. An example of such a graph is given in Fig. 2.3-11.

These graphs, together with the experimentally determined (and tabulated) coefficients which link the water:(cement + fly ash) ratio to the concrete strength (Abram's equation), provide a relatively simple way of selecting the optimum mix proportions for a fly ash concrete having comparable performance with reference plain concrete.

Again, as in the case with Cannon's method, the applicability of Ghosh's method is limited by the fact that it relies on the relationships established for a particular set of materials. In the conclusion of his paper Ghosh stated: "The curves and constants given in this paper are only applicable to Ontario Hydro's Lakeview fly ash produced during the period of January 1972... If any other fly ash is used, because of its effects on strength, water requirements, and admixture

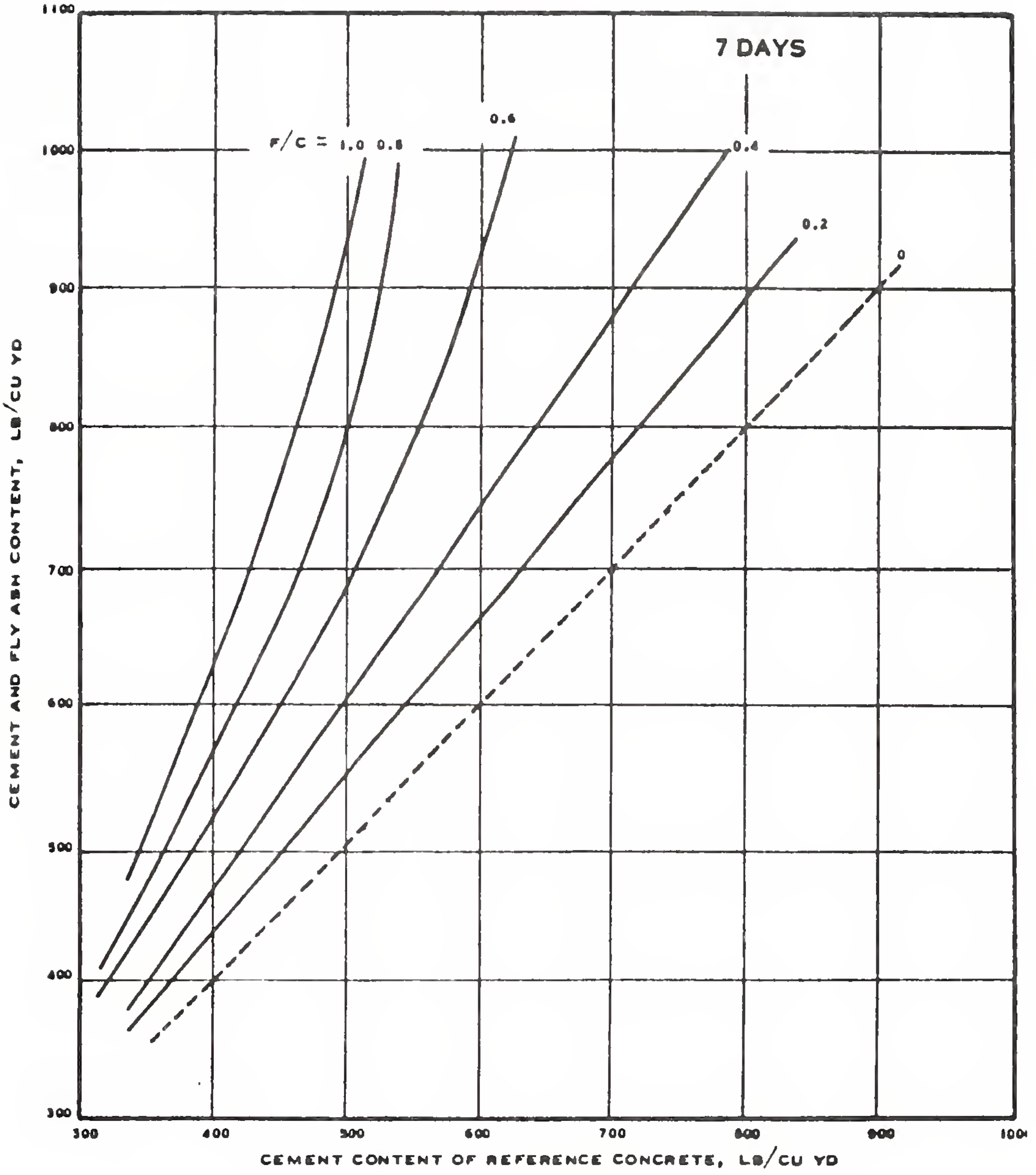

Figure 2.3-11 Cement plus fly ash content vs. cement content for equal 7 day strength [184].

dosage, a pilot series must be performed so that suitable correction factors can be applied to the constants in the equations."

Analysis of Figure 2.3-11 suggests another drawback of the proposed method. At high cement contents of the reference concrete, i.e. where high strengths are required, the method forces a reduction in the allowable level of fly ash replacement. In current practice, high strength concretes are often achieved with high levels of cement replacement with selected fly ashes.

A few other MRMs of fly ash concrete mix design have been proposed in addition to those discussed above [185-187]. All of them recognize the fact that in order for a fly ash concrete to achieve an early age strength comparable with that of plain concrete, the amount of a fly ash added to the mix has to be greater than the amount of cement removed. Of these, the method proposed by Popovics [187] differs from others (including the ones discussed previously) by presenting a theoretical rather than an empirical approach to the problem of fly ash concrete mix proportioning.

Popovics proposed a theoretical formula for the relationship between composition and strength of concrete containing fly ash.

The formula suggested, although somewhat similar to the modified Abrams relationships discussed previously, can be directly applied in the fly ash concrete mix design process without the necessity of establishing many independent parameters. This is due to the fact that the proposed equation employs only one variable (weight of fly ash as a percent of cementitious material) whereas all other parameters, although empirical, are independent of the fly ash content.

Using this approach, one can calculate the amount of the cementitious material needed for a specified standard compressive strength at the age of 28 days for a given concrete consistency. Unfortunately, the equation does not address the problem of change in mix water requirements brought about by the type and amount of the fly ash used.

Popovics used his equation to calculate fly ash concrete mix proportions for different values of 28 day strengths, and compared his results with empirical data obtained previously reported by various researchers (including the previously discussed works of Washa [108], Cannon [112], and Ghosh [184]). Although the calculations were done with the simplifying assumption that the water needed for a specified slump is independent of the cement and fly ash content, it appears that the experimental data support the predicted values quite well. This suggests that such a theoretical approach has some general validity, although undoubtedly much broader experimental support would be welcome.

In general, all of the mix design procedures presented above have overcome the problem of lower early age strength of fly ash concrete associated with previously discussed SRMs of mix proportioning. In other words, application of MRMs can result in fly ash concrete with strengths equal to those of the plain portland cement concrete at any desired age. In all cases the fly ash concrete mix will have total cementitious material content larger than comparable mix without a fly ash. The appropriate yield of the mix is assured by adjusting the aggregate content.

The broader application of Modified Replacement Methods is limited by a number of practical problems. Although capable of assuring equivalent strengths at earlier ages, the MRMs do not address the uniqueness and variability of fly ash properties. Most of the methods are based on modification of a reference plain concrete mix, by replacing a portion of the cement with slightly larger amount of a given fly ash. Such an approach limits the possible applicability of the design method to a set of materials with properties similar to the ones used during its development. Even in this case, the design process remains mostly trial-and-error in nature. The workability and water demand of the fly ash concrete, both strongly influenced by the physical and chemical characteristics of a given specific fly ash, are likely to be difficult to control with these methods of mix proportioning. These properties, if not properly taken into account, can have a very pronounced effect on the durability of concrete.

As mentioned earlier, in using any of the MRMs, the amount of fly ash added is always in excess of the amount of cement removed. A method which takes this to the limit is sometimes used for proportioning fly ash concretes. This so-called "Addition Method" of mix design requires a direct weight addition of the fly ash to cement without any reduction of the cement content itself. Since this causes a substantial increase in the cementitious content of the mix, an adjustment is usually made in the aggregate content (sand or coarse aggregate, depending on the nature of a particular job) in order to adjust the yield.

The addition method is generally used to improve workability or reduce bleeding of lean concrete. This method might be especially useful in low strength or superplasticized concretes [188].

2.3.3 Rational Methods

The driving force behind development of so called rational methods (RMs) of fly ash concrete mix proportioning was the claim that neither SRM or MRM methods fully utilized the potential advantages and versatility which the use of fly ash can provide. It was advocated that by recognizing and accommodating the unique characteristics of a particular fly ash in the mix proportioning and production procedures, one can assure more effective use of this material. In other words, one should quantify the influence of fly ash on various concrete properties and utilize that quantification at the design stage.

In RM methods, this quantification is universally achieved by employing a so called "cementing efficiency factor". In this approach each fly ash is assumed to have the ability to increase concrete strength by an amount proportional to that produced by the equivalent weight of cement. The efficiency factor is the constant of proportionality for a given fly ash. Such an assumption allows fly ash to be treated essentially as a low grade cement, and permits its influence on strength (and related properties) to be quantified in terms of an equivalent water:cement ratio.

The "fly ash cementing efficiency factor" (K) was first introduced in 1967 by Smith [189], who defined it as a weight (F) of fly ash equivalent (in terms of strength) to a weight (KF) of cement. In other words, the cementing efficiency (K) may be considered as the ratio of the weight of cement which would produce a given increase in compressive strength to the weight of a fly ash which would produce a similar increase in strength.

Although this factor is assumed to be unique for each fly ash, after the first series of tests Smith [189] concluded that "a value of 0.25 for K might be a reasonable one on which to base a rule for the design of fly ash concrete to reach a desired strength". The initial step in Smith's design procedure is the proportioning of plain concrete mixes covering the wide range of strengths. The compressive strength of those concretes is than tested at a given age and the results are used to plot respective strength vs. w:c ratio curves. In a next step, a value for K is assumed to be 0.25, and corresponding fly ash mixes are proportioned using the Abram's equation and an adjusted w:c ratio.

The adjusted w:c ratio is calculated from the relationship:

$$W = W_s[1/(1+KF)]$$

in which:

W = w:c ratio of fly ash concrete, by weight

W_s= w:c ratio of a plain concrete mix for the desired strength, by weight

K = cementing efficiency of a specific fly ash

F = fly ash-cement ratio, by weight

Again, the strength results are plotted vs. the w:c ratio of a fly ash concrete. These two sets of curves are shown in Fig. 2.3-12. Comparing these two curves, one can determine the value of w:c ratio (on a plain concrete curve) which will yield the same strength as the fly ash concrete. Substituting that value of w:c ratio into the above equation, one can back-calculate the actual value of K and use it to proportion the fly ash concrete.

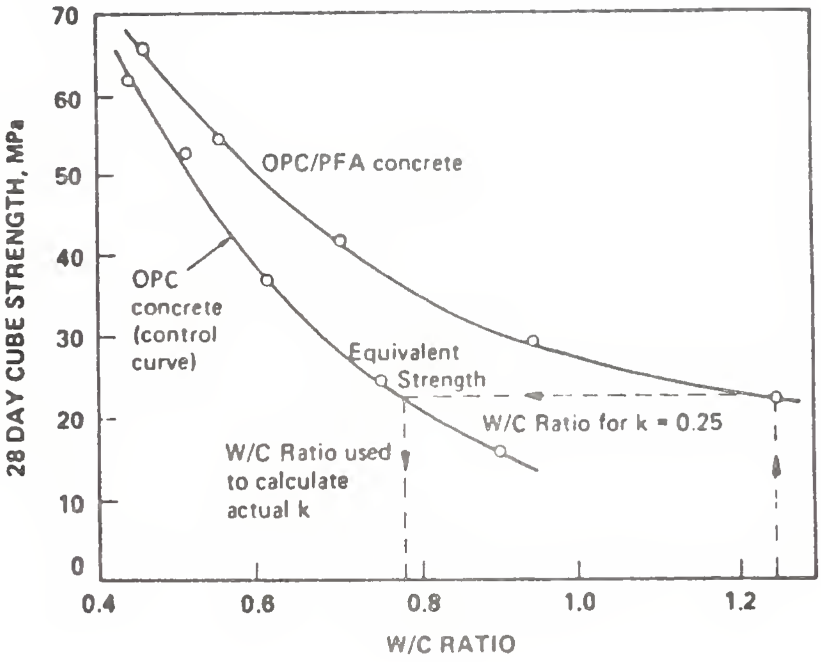

Figure 2.3-12 Typical relationship between strength and water/cement ratio for plain (OPC) and fly ash (OPC/PFA) concretes (from reference [189]).

As seen from the above, the proposed procedure is quite complex and requires a large number of batches for both plain and fly ash concretes. It also depends entirely on strength as a controlling parameter in the design.

In order to simplify the proportioning process Miles [190] prepared a series of charts to aid the designer. However, the problem is further complicated by the fact that the value of K has been found to vary depending upon the cement used [191], the curing conditions employed [192], and the nominal strength level to which the concrete is being proportioned [193]. An equally important complication is the fact that the method does not account for the differences between the water demand of cement and that of combined cement-fly ash mixture, and therefore does not provide for the most effective and practical use of fly ash. In order to overcome this deficiency Rosner [194] proposed yet another procedure incorporating in his method some of the concepts from Cannon [112] and from Smith [189]. Unfortunately, such an approach further complicates the design process, and therefore Rosner's proposal appears to be unsuitable in practice.

Another method similar in concept to Smith's procedure was developed by Dunstan [195]. In his method Dunstan used a series of theoretical equations which, when supplemented by a limited series of trial mixes, should allow the designer to judge the influence of a particular fly ash on the strength and durability of the concrete. The crucial parameters in these equations are cement efficiency (C_e), fly ash efficiency (F_e), and efficiency index (E). The author separated the strength produced by the portland cement from the strength produced by the fly ash, and defined the efficiency of each of those ingredients as being the strength produced for each pound of the material used. Therefore the efficiency of cement can be written as follows:

$$C_e = S_c / C_w$$

where (C_e) is the cement efficiency, (S_c) is the strength produced by the cement, and (C_w) is the weight of cement per cubic yard.

Similarly, the efficiency of fly ash can be written as follows:

$$F_e = S_f/F_w$$

where (F_e) is fly ash efficiency, (S_f) is the strength produced by the fly ash, and (F_w) is the weight of a fly ash per cubic yard.

The strength (S_f) produced by the fly ash is defined as the strength in excess of the strength produced by the cement alone, and can be expressed as follows:

$$S_f = S_{c+f} - S_c$$

where (S_{c+f}) is the total strength produced by the cement and fly ash.

In order for the method to work, the values of (S_{c+f}) and (S_c) have to be known. While the first of those two terms is determined from the experimental data, the author proposed that the value of the second term be calculated from Feret's equation, which theoretically predicts the strength of plain concrete as a function of its volumetric composition.

The efficiency index (E) is defined as the ratio of the efficiency of fly ash (F_e) to the efficiency of cement (C_e) as shown below.

$$E = F_e/C_e$$

The value of this efficiency index varies with the percentage of a given fly ash, and these changes can be described by the relationship $(1-f)^n$, where (f) is the percent (decimal) of fly ash. In addition, the value of (n) will be a function of the chemical composition of the fly ash.

Dunstan suggested the following values of n (for minimum age 28 days):

Class F Ash	n = 0.50 to 2.00
Class C Ash	n = 0.15 to 1.00

In physical terms the n-value is the measure of the reaction of fly ash with the by-products of a cement hydration (hydrated lime and alkalies).

In order to use Dunstan's method in practice, one has to determine the values of two unknowns (E and n), and therefore at least two (but preferably three) trial mixes are required. Once those unknowns are determined, the strength, cost, and durability - related calculations can be performed using the set of equations provided by the author.

The method has been tested by Dunstan for a few cases and seems to be able to model the strength and durability of fly ash concrete well. However, as any method which mixes empirical parameters with theoretical values, this particular procedure is not only complicated but also of limited applicability. It lacks any provision for variation of the water demand among different fly ashes; in fact it assumes that the water requirement either stays constant or is reduced by fly ash addition. Nor does it have any provision for the effect of chemical admixtures.

These limitations, along with the heavy reliance of the method on theoretical equations for predicting the strength of the reference concrete, make Dunstan's procedure unsuitable for general application.

Of the other RMs of fly ash concrete mix design available, the quickest and most practical approach is that proposed by Munday et al. [171]. This method allows one to produce a mix with specified strength and workability without direct reference to a reference plain concrete mix, and with a minimum number of trials, providing that records indicating the performance characteristics of the particular fly ash are available.

Where such information does not exist, the method will initially require a considerable input of data for a given fly ash source. The authors of the method provided these initial data for six different fly ashes, covering a wide range of characteristics. The necessary information is conveniently organized in the form of graphs and tables. Once this information has been established, the process of selecting mix proportions reduces to the following six steps:

- determination of water:cement ratio;
- selection of free water content;
- determination of fly ash:cement ratio;
- determination of cement and fly ash content;
- determination of total aggregate content;
- examination of trial mixes.

The method is advocated as suitable for use with any type of fly ash but in order to achieve sufficient cement savings, the water demand of a fly ash must not be greater than that of the cement used.

3.0 MATERIALS

3.1 Selection of Fly Ashes

Fly ashes from five different power plants were selected for use in this project so as to represent a wide range of chemical and physical properties of ashes available in Indiana. Four of the five ashes were obtained from sources of fly ash studied in the previous project, although the actual fly ashes, sampled in 1985, are not exactly the same materials as those sampled in 1983.

The fly ashes used in the present project are from sources as follows:

(a) The Schahfer Station of the Northern Indiana Public Service Corp., here designated F1, and corresponding to the ash coded NIP-1 of the earlier investigation.

(b) The Stout Station of the Indianapolis Power and Light Co., here designated F2, and corresponding to the ash coded IPL-1 of the earlier investigation.

(c) The Gibson Station of Public Service Indiana, Inc., here designated F3 and corresponding to the ash coded PSI-2 of the earlier investigation.

As indicated in the coding, the three fly ashes above are Class F fly ashes with low contents of CaO. The other two ashes are of higher CaO content and are considered as Class C fly ashes. These consist of ashes from the following sources:

(d) The Mitchell Station of the Northern Indiana Public Service Corp., here designated C1 and corresponding to the ash coded NIP-2 of the earlier investigation.

(e) The Rockport Station of the Indiana and Michigan Electric Co., here designated C2.

The Rockport Station came on stream after all samples had been collected for the preceding project and was thus not included in that earlier study. It was added to the present study because of its widespread present use in concrete in Indiana and because it is a somewhat more typical Class C fly ash than ash C1; the latter has extremely high contents of both CaO (37.1%) and MgO (9.8%), and its properties may not be typical of common Class C fly ashes in Indiana.

The important chemical and physical properties of all of these ashes are given in Table 3.1-1. Table 3.1-2 summarizes their mineral compositions and Table 3.1-3 provides characteristics of their glass components.

The analyses of Table 3.1-1 are generally similar to but not identical with those reported for corresponding ashes from the same sources in the report of the earlier project. This is not surprising since there was an interval of approximately 3 years between the period of sampling of that of the earlier project and that of the present one.

Among the more important differences that might be pointed out are the following:

(1) For the F1 ash, the present material is significantly coarser than the earlier NIP-1 sampling (mean size 19 μm as compared to 3 μm),

Table 3.1-1 Chemical and physical data for fly ashes used in concretes.

Generating Plant	Schahfer	Stout	Gibson	Mitchell	Rockport
Symbol Used	(F1)	(F2)	(F3)	(C1)	(C2)
SiO_2 (%)	59.9	49.8	48.2	21.4	35.8
Al_2O_3 (%)	23.7	22.9	22.0	14.1	19.6
Fe_2O_3 (%)	5.73	21.0	16.0	9.9	6.36
SiO_2+Al_2O_3+Fe_2O_3 (%)	89.3	93.7	86.2	45.4	61.80
CaO (%)	1.69	4.14	1.79	37.1	26.80
MgO (%)	1.20	0.85	1.90	9.80	3.30
Loss on Ignition	2.43	3.40	6.50	1.14	0.42
% Soluble Na_2O	0.14	0.08	0.20	0.14	0.02
% Soluble K_2O	0.12	0.01	0.05	0.01	0.004
% Total Na_2O	0.50	0.25	1.31	0.60	1.32
% Total K_2O	0.55	2.75	2.27	0.60	0.73
Pozzolanic Activity Index with cement (%)	136	57	78	110	116
% of Magnetic Particles	1.6	20.1	12.6	1.50	0.60
Specific Gravity	2.00 (?)	2.37	2.35	2.75	2.61
Mean Size, µm	19	26	16	17	14
% > 45 µm	2	31	24	12	21

Table 3.1-2 Mineralogies of the fly ashes.

Component Present	Type of Fly Ash				
	F1	F2	F3	C1	C2
C_3A				+?	+?
CaO				+	+
Anhydrite			+	+	+
Gehlenite		+			
Hematite	+	+	+	+	+
Maghemite	+	+	+	+	
Magnetite	+	+	+	+	
Mullite	+	+	+		
Periclase				+	+
Quartz	+	+	+	+	+

Table 3.1-3 Characteristics of glass present in fly ashes.

Fly Ash	Glass Characteristics
F1	Glass with unusually high content of silica (tridymite type). X-ray diffraction pattern shows intense glass band centering at about 23° 2Θ (Cu radiation).
F2	Siliceous glass (tridymite type). Substantial glass band present with maximum at approximately 24° 2Θ (Cu radiation).
F3	Siliceous glass (tridymite type). Relatively intense glass band present in the x-ray pattern, indicative of the larger than usual glass content. The maximum of the band is located at about 24° 2Θ (Cu radiation).
C1	Glass basically siliceous in structure but strongly modified by an increased calcium content. X-ray diffraction pattern is characteristically symmetrical and centered near 27° 2Θ (Cu radiation).
C2	Calcium aluminate glass with characteristically asymmetrical pattern and maximum centered near 32° 2Θ (Cu radiation).

(2) For the F3 ash, the loss on ignition is much higher (6.5% as compared with 1.2%),

(3) For all of the ashes, the content of magnetic particles is much less (by a factor of two or more) than those reported for the earlier samplings.

In general the chemistry of each ash is fairly similar to that of the corresponding ash in the earlier sampling, and other characteristics such as the pozzolanic activity index are also quite similar.

It should be pointed out that the present C1 ash, like the earlier ash sampled from the same source, technically does not qualify as an "official" Class C pozzolan according to the present specification. The present ASTM C 618 specification requires a combined SiO_2 + Al_2O_3 + Fe_2O_3 content of at least 50%; the total recorded here is only 45.4%.

A discussion of some of the specific features of the analyses for each of the five fly ashes used is provided below.

The F1 fly ash was collected from Unit 15 of Schahfer power station in Jasper County, Indiana. This unit burns bituminous coal. As seen from Table 3.1-1 this particular fly ash has a low content of CaO (1.7%) and an unusually high content of SiO_2 (60%). The contents of others elements are rather typical for this type of fly ash. The Pozzolanic Activity Index with cement (PAI) was 136%, which was higher than that for any other fly ash used in this project. Although its mean particle size (19 µm) is about average for fly ashes, this particular fly ash has an unusually low content of oversized (>45 µm) material, only 2%.

Fly ash F2 was collected from a silo serving No. 700 boiler in the Stout Generating Station in Indianapolis, Indiana. This fly ash is derived from an Illinois Basin sub-bituminous coal. The chemical analysis shows that it contains an unusually high percentage of Fe_2O_3 (21%), and a high percentage of particles coarser than 45 µm (31%). The PAI is only 57%, which is the lowest value of the fly ashes used in this study, and is lower than the 75% minimum value recommended for fly ash in ASTM C 618. Despite the high iron content, the specific gravity of this fly ash is only 2.37, suggesting the presence of a significant amount of a hollow or partly hollow particles.

Fly ash F3 comes from the Gibson Power Station in southwest Indiana, and was collected from the ash transfer line serving Units 3 and 4 of this station. It is a low calcium fly ash with rather typical chemical composition. The proportion of the magnetic particles is high but not excessive (12.6%), and roughly corresponds to the analytical content of Fe_2O_3, which is 16%. This fly ash also has a high content of oversized material, 24%.

The C1 fly ash was supplied by the American Fly Ash Company, Des Plaines, IL, and was collected from the Mitchell Station located in Lake County, northwest Indiana. It has a very high CaO content (37.1 %) and an extremely high MgO content (9.8%). This ash has the highest specific gravity of all of the fly ashes studied, 2.75. Since it only has a moderate iron oxide content (9.9%), it is suspected that the particles are almost entirely solid. The high value of PAI (110%) indicates potentially good reactivity.

The C2 fly ash was also supplied by the American Fly Ash Company and was obtained from Unit I of the Rockport Power Station in southern Indiana. It has a CaO content of 26.8%, placing it clearly in the high calcium fly ash group. The iron oxide and MgO contents of this fly ash are fairly low (approximately 6% and 3% respectively), and the PAI is 116%, indicative of excellent reactivity. The mean particle size of this fly ash is relatively fine (11 µm) but despite this, the content of > 45 µm particles is high (21%).

Despite individual differences, the data provided in Tables 3.1-1 to 3.1-3 reflect certain patterns which are distinctive for low calcium vs. high calcium ashes. For the low calcium fly ashes the combined content of silicon, aluminum and iron oxides is close to 90%. The CaO content of these ashes is low and varies from 1.7% to 4.1%. Two of the ashes (F2 and F3) have substantial amounts of Fe_2O_3. The content of Al_2O_3 is relatively constant for all three ashes (22 to 24%), but the content of SiO_2 is significantly higher for fly ash F1 (about 60%) than for F2 and F3 (both about 49%).

The immediate difference between the high calcium fly ashes and the low calcium fly ashes used in this study is the high amount of CaO present in the former (37% and 27% for fly ashes C1 and C2 respectively). These ashes also have only about half of the silica that the low calcium fly ashes have, and less alumina.

Finally, the MgO contents of the low calcium fly ashes are quite small, but both the high calcium fly ashes show substantial amounts of this component.

The analysis of the x-ray diffraction patterns reveals that all the low calcium fly ashes contain such mineral components as hematite (Fe_2O_3), magnetite (ferrite spinel - Fe_3O_4), mullite ($3Al_2O_3 \cdot 2SiO_2$), and quartz (SiO_2). All of these ashes also yield intensity band maxima (associated with the presence of glass) symmetrical around 23° 2Θ (Cu radiation), which is approximately the position of the main tridymite (SiO_2) peak.

The mineralogy of high calcium fly ashes is considerably different from these. In both C1 and C2 fly ashes the cementitious and possibly cementitious crystalline compounds are present including crystalline

CaO, anhydrite, and possibly C_3A. Neither of these fly ashes shows the presence of mullite, but both contain periclase.

Quartz and hematite were the only crystalline components common to all of the fly ashes examined.

Since the high calcium fly ashes have high CaO contents, the glass band maxima are shifted toward higher values of 2Θ angle. For the C1 fly ash the glass seems to be basically siliceous in structure but strongly modified by a high calcium content. The band is roughly symmetrical, but it is centered near 27° 2Θ (Cu radiation). The band for fly ash C2 is characteristically asymmetrical, with a maximum centered near 32° 2Θ (Cu radiation), which is the position of the largest peak for the compound $C_{12}A_7$.

3.2 Portland Cements

When selecting the cement for use in this research an attempt was made to choose materials which would represent typical cements used in highway construction projects in the state of Indiana. Consultation with personnel of the Indiana Department of Highways indicated that while the types and compositions of cements used in field construction projects do vary locally within the state, the overall differences are not very significant. Two sources of cement, one being primarily used in northern and eastern part of the state, and the other used mainly in the central and southern part, were selected for use in this investigation.

The cement coded "L" is a product of the Greencastle, IN plant of Lone Star Industries, lnc; that coded "S" was produced at the Fairborn, OH plant of Southwestern Portland Cement Co., Inc. Both are Type I cements without noteworthy peculiarities.

The chemical compositions and physical characteristics of these cements are provided in Tables 3.2-1 and 3.2-2 respectively. All of the reported values, except the potential compound composition of cement S, were determined by the cement manufacturers and supplied at the time of material shipment.

The composition of cement L is in the middle of the normal range for Type I cements, and contains about twice as much Al_2O_3 as it does Fe_2O_3. As the result the potential C_3A content calculated using the Bogue equation is a little more than 10%. This is higher than in some Type I cements, but not unusually high.

The analysis of cement S shows an unusually high content of MgO, 5%. The amounts of other oxides present in cement S are reasonably typical for Type I cement except that, at 60.6%, the content of CaO is on the low side of the normal range.

In cement S the contents of Al_2O_3 and Fe_2O_3 do not differ from each other by as much as they do in cement L, and the potential amount of C_3A is only about 6% (see Table 3.2-1). Also, cement S shows a lower percentage of C_3S than cement L. The combination of these factors would suggest that the early age reactivity of cement S might be expected to be less than that of cement L.

This is consistent with the higher setting time exhibited for this cement as indicated in Table 3.2-2. The apparently lower early reactivity is shown despite the fact that this cement has higher Blaine fineness than cement L (388 m^2/kg as compared with 327 m^2/kg).

Table 3.2-1 Chemical composition of cements used in this study.

Chemical Analysis (%)	Type of Cement	
	Cement "L"	Cement "S"
SiO_2	20.98	20.20
Al_2O_3	5.38	4.50
Fe_2O_3	2.46	3.40
CaO	64.34	60.60
MgO	1.09	5.00
SO_3	3.03	2.80
Na_2O	0.09	0.25
K_2O	0.72	0.90
Alkalies, Eqv. Na_2O	0.56	0.84
Loss on Ignition	1.40	1.70
Insoluble Residue	0.23	0.42
Potential Compound Composition, Bogue, (%)		
C_3S	54.14	50.50*
C_2S	19.39	19.80*
C_3A	10.10	6.20*
C_4AF	7.47	10.40*
$CaSO_4$	5.15	4.80*

* calculated by the authors

Table 3.2-2 Physical characteristics of cements used in this study.

Physical Data	Type of Cement	
	Cement "L"	Cement "S"
Specific Surface: (cm^2/g)		
Blaine	3275	3880
Wagner	1730	--
Fineness: (#325, % passing)	83.7	--
Soundness:		
Autoclave Expansion (%)	0.011	0.220
Normal Consistency: (%)	25.0	--
Time of Setting:		
Gillmore Initial (hr:min)	1:55	--
Gillmore Final (hr:min)	3:50	--
Vicat Initial (hr:min)	1:25	2:08
Vicat Final (hr:min)	3:00	4:30
Air Entrainment: (% by volume)	9.7	9.4
Compressive Strength: (psi) (2-inch mortar cubes)		
1-day	2140	2040
3-days	3430	3230
7-days	4290	4130
28-days	5380	5360

3.3 Aggregates

Section 501 entitled "Portland Cement Concrete Pavement" and Section 702 entitled "Structural Concrete" of the Indiana Department of Highways (IDOH) Standard Specifications [196] state that portland cement concrete for use in pavements or other highway-related structures should be produced with coarse aggregate of size No. 5 or No. 8 and fine aggregate of size No. 23.

It was found that concrete made with coarse aggregate of size No. 8 (d_{max} = 1.0 in.) was difficult to mix in the laboratory concrete mixer available for use in this project. Accordingly, the next finer size in the specifications, No. 9, with d_{max} of 3/4 in., was substituted.

The coarse aggregate used was clean crushed limestone supplied by Verplank Concrete and Supply Inc., of West Lafayette, IN. The grading and selected physical properties of this aggregate are shown in Table 3.3-1, which also provides the aggregate gradation limits of size No. 9 according to the IDOH specification. As seen from the table, the grading of the coarse aggregate used complies with the specification requirements except that 1% of the material is retained on the 3/4 in. sieve.

The bulk specific gravity (SSD) of the coarse aggregate, determined according to ASTM C 127 [198] was 2.69, a typical value for limestone aggregate. The absorption was 1.35%.

The fine aggregate used in this study was a local siliceous pit sand. Its physical characteristics and sieve analysis data are given in Table 3.3-2, which also provides the required sand gradations according to the IDOH specification. As can be seen, the sand used satis-

Table 3.3-1 Physical properties and gradation of fine aggregate.

Fineness Modulus FM = 3.0
Bulk Specific Gravity (saturated surface dry) $BSG_{SSD} = 2.63$
Dry Rodded Unit Weight DRUW = 96.1 lb/cu ft
Absorption A = 1.83%

Sieve	Cumulative weight percent		IDOH Standard Specifications Sect. 903.01 - Grading Requirements for Fine Aggreg. No.23 (% passing)
	Retained *	Passing *	
3/8 "	0	100	100
No. 4	1	99	95-100
No. 8	16	84	80-100
No. 16	35	65	50-85
No. 30	57	43	25-60
No. 50	88	12	5-30
No.100	99	1	0-10
Pan	100		
Fineness Modulus	3.0		

* Average of 6 independent tests

Table 3.3-2 Physical properties and gradation of coarse aggregate.

Bulk Specific Gravity (saturated surface dry) $BSG_{SSD} = 2.69$
Dry Rodded Unit Weight DRUW = 96.2 lb/cu ft
Absorption A = 1.35%

Sieve	Cumulative weight percent		IDOH Standard Specifications Sect. 903.02 - Grading Requirements for Fine Aggreg.
	Retained *	Passing *	No. 9 (% passing)
1"	0	100	100
3/4"	1	99	100
1/2"	18	82	60-85
3/8"	56	44	30-60
1/4"	88	12	---
No.4	96	4	0-15
Pan	100	0	

* Average of 6 independent tests

fies the requirements for No. 23 sand with regard to gradation curve. However, the calculated value of its fineness modulus is 3.0, a number indicating a coarse gradation uncomfortably close to the 3.1 upper limit allowed by the ASTM standard specification C 33 [197].

The values of absorption (1.83%) and bulk specific gravity (2.63) were both typical for this type of fine aggregate.

The moisture content of all aggregate was adjusted to the approximate SSD conditions before batching, in order to comply with the requirements of the mix design method and to avoid undesirable variability. Immediately prior to the mixing a hot plate was used for a quick check of the actual moisture present. If necessary, additional water was added to the aggregate and mixed for 5 minutes in order to ensure that SSD condition was maintained in all cases.

The sand and coarse aggregate were combined at a S/(S + CA) ratio of 0.46 by weight. This ratio was found in separate trials to produce the combination with the maximum packing density.

3.4 Admixtures

To minimize the number of variables only one type of air entraining agent, neutralized vinsol resin (Master Builders MBVR) was used as the air entraining admixture. The quantity of air entraining agent was adjusted as necessary to give 6.0 ± 0.75% of air in the fresh concrete mix, after correction for the aggregate void content.

4.0 EXPERIMENTAL PROCEDURES USED IN CONCRETE STUDIES

This chapter describes the experimental procedures used in the course of the investigations on concrete carried out in this project. Some of the more specialized procedures used in examination of the properties of cement pastes and in investigations of the properties of fly ashes themselves are not included here, and in most cases are summarized in the individual sections where the results are described.

The methods used in the studies on concrete were for the most part the straightforward ASTM procedures commonly used in the testing laboratories dealing with construction materials. For such methods, only a brief description of the procedure is provided. In cases where the test method was not a standard ASTM procedure, or for less commonly used standard methods, an attempt was made to provide as detailed a description as necessary in order to permit the measurement to be duplicated elsewhere.

4.1 Properties of the Aggregates

Standard ASTM procedures were used in determining the properties of the aggregates. These determinations included (1) particle size distribution of sand and coarse aggregate using ASTM C 136-80 [199], (2) bulk specific gravity and absorption of coarse aggregate using

ASTM C 127-80 [198], (3) bulk specific gravity and adsorption of fine aggregate using ASTM C 128-79 [200], and (4) dry rodded unit C 29-78 [201].

The fineness modulus of sand was calculated using the sum of cumulative percentages retained on the 3/8-in. and Nos. 4, 8, 16, 30, 50, and 100 sieves respectively, divided by 100.

4.2 Foam Index Test For Fly Ash

In order to assess the influence of specific fly ash used on the amount of air entraining admixture (AEA) required for a given fly ash-cement combination, the "Foam Index" test was used. This test, originally proposed by Dodson [202], was later significantly modified [203-205]. The version adopted for the present study was the most recent modification proposed by Day et al. [205], which contains features of all of the previous procedures.

The apparatus for the foam index test consisted of a wide mouth 400 ml capacity glass jar with height-to-diameter ratio of approximately 2.0. At the beginning of the test, 50 ml of water was placed in the jar and pre-mixed with 20 g of cement (reference mixes) or with a hand mixed blend 17 g of cement and 3 g of fly ash (for 15% replacement level), or 15 g of cement and 5 g of fly ash for 25% replacement level. The jar was than capped and shaken vigorously for 15 seconds. Next, the AEA solution (AEA diluted 8:1 by volume with water) was added one drop at a time, using an eye-dropper. The dropper used was tested repeatedly for volume dispensed per drop, and was shown to deliver 0.031 ml of the liquid reproducibly. After each addition, the jar was vigorously shaken for an additional 15 seconds, and than left to stand for 45 seconds. The lid was then removed and the visual determination of the uniformity and stability of the foam and bubbles was carried out.

If the bubbles remained over the entire cross sectional area of the jar, and there were no observable discontinuities, the foam was considered to be stable. At this stage the test was terminated and the amount of AEA (total number of drops) required to produce such state was recorded as the Foam Index (FI). If discontinuities were observed in the foam, the foam was recognized as being in an unstable state. In such a situation, an additional drop of AEA solution was added and the shaking procedure was repeated. This drop-wise addition and testing was repeated until a stable foam was exhibited.

4.3 Preparation of Pastes

All of the pastes used in this study were prepared using cement "L". Separate pastes were prepared containing this cement and each of the five previously described fly ashes, and a reference paste was prepared containing only the cement. All of the pastes were made using the same water:solids ratio as used in the concrete, 0.49, using deionized water. Fly ash was used at the 25% replacement level throughout. The actual composition of each paste batch is given in Table 4.3-1.

Table 4.3-1 Components and proportions of pastes used in the study

Mix	Fly Ash Type	Replacement Level (%)	Weight of Components (g)		
			Water	Cement	Fly ash
L	----	----	462	939	----
LF1(25)	F1	25	457	711	220
LF2(25)	F2	25	437	680	212
LF3(25)	F3	25	435	677	213
LC1(25)	C1	25	429	666	208
LC2(25)	C2	25	408	634	200

A standard Hobart mixer (model N-50, capacity 4.73 dm^3) was used in mixing the pastes. The ASTM C 305 Standard Method for Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency [206] was followed in preparation of the pastes.

After all the mix water was placed in the bowl of the mixer, the cementitious material was added, and a period of 30 seconds was allowed for the absorption of the water. This was followed by mixing at low speed (145 ± 5 rpm) for 30 seconds, and a waiting period of 15 seconds. During this waiting period the paste was scraped down from the sides of the bowl. The mixing was then continued for additional 1 minute at medium speed (285 ± 10 rpm).

Immediately after mixing the paste was cast into plastic cylindrical jar molds of 5.1 cm diameter and 6.5 cm height, compacted, and sealed. A total of six cylinders were cast from each batch. Two were used in the determination of heat evolution, one in the determination of setting time, one in measuring the non-evaporable water content, one for determining the calcium hydroxide content, and one for expression of pore solution. All of the samples were stored and tested in the laboratory environment (temperature about 23° C and RH about 75%). Only setting time and heat evolution procedures are reported here; the other measurements were carried out separately and will be reported elsewhere.

4.4 Setting Time of Pastes

The setting time of the pastes was determined using the standard Vicat apparatus. The criteria for determining the initial and final set complied with ASTM C 191 section 6.2 [207]. The procedure actually used in the course of the test differed from the ASTM routine in two ways: the paste specimen remained in its jar rather than being placed into the prescribed conical ring, and the pastes tested were prepared at constant water:solids ratio, not at constant consistency, as specified by C 191.

4.5 Setting Time of Concrete

The setting of concrete mixes was investigated using the ASTM C 403 penetration resistance procedure [208]. In this method the time of set of concrete is determined by testing mortar sieved from the concrete mix through the No. 4 (4.75-mm) sieve. This separation of the coarse aggregate is done in order to eliminate the interference of the large pieces of aggregate with the penetrometer needle, therefore assuring more reproducible results.

The mortar obtained as a result of sieving was remixed by hand,

and than placed in cylindrical metal containers, 6 in. in height and 6 in. in diameter. Each container was then filled to a depth of 5½ in. and covered with a tight-fitting plastic cover, which was removed only when measurements were being made. The half-inch space between the mortar surface and the top of the container served as a reservoir for collection of bleeding water. Three replicate mortar specimens were prepared for each concrete tested.

The apparatus used in the study was a standard Proctor Mortar Penetrometer Model CT-426, manufactured by Soiltest, Inc. The instrument is a spring reaction-type apparatus, with pressure gage of 200 lbf capacity, and meets the requirements of ASTM Specification C 403.

The general procedure described in C 403 was followed when making the measurements of the setting time. Just prior to making the penetrometer test a plastic syringe was used to remove the bleeding water from the surface of the specimen. A penetrometer needle, of appropriate size depending on the state of hardening of the mortar, was inserted in the apparatus, and a constant vertical force applied to cause penetration until the needle penetrated the mortar to a depth of 1 in.

Initial readings were taken approximately 3 hours after first contact of cementitious material and water, and subsequent readings were taken at intervals ranging from 1 hour to about 20 minutes, depending on the pattern of observed increase in penetration resistance of the mortar.

The force of resistance offered to the penetration of the needle was measured on the penetrometer gage in lbs., and the steady pressure required to cause the penetration to continue to a maximum depth of 1.0 in. was computed by dividing the force applied by the normal cross-sectional area. In compliance with the recommendations of ASTM C 403, the time required for the mortar to reach a penetration resistance of 500 psi was taken as the time of initial setting, and the time to reach 4000 psi resistance was taken as the time of final setting.

4.6 Temperature Evolution

The change in temperature occurring as a function of time for the first 14 hours or so of hydration was determined for the previously described hydrating pastes (see section 4.3) under quasi-adiabatic conditions. The apparatus used in this study consisted of a styrofoam insulating box, two plastic containers (one for the paste under study and the other for a reference material), a set of two matched thermistors, a Wheatstone bridge and a strip-chart recorder.

A schematic view of the apparatus and the test set-up is shown in Fig. 4.6-1.

In this method, in order to electronically cancel out fluctuations in the external temperature and humidity, the thermistor embedded in cement paste is matched against another thermistor embedded in an inert reference material, 20-30 mesh Ottawa sand mixed with water. The water:sand ratio used was the same as water: cementitious material ratio of the pastes under study.

Immediately after the paste was prepared it was cast into the plastic specimen jar, and capped with a lids containing openings for

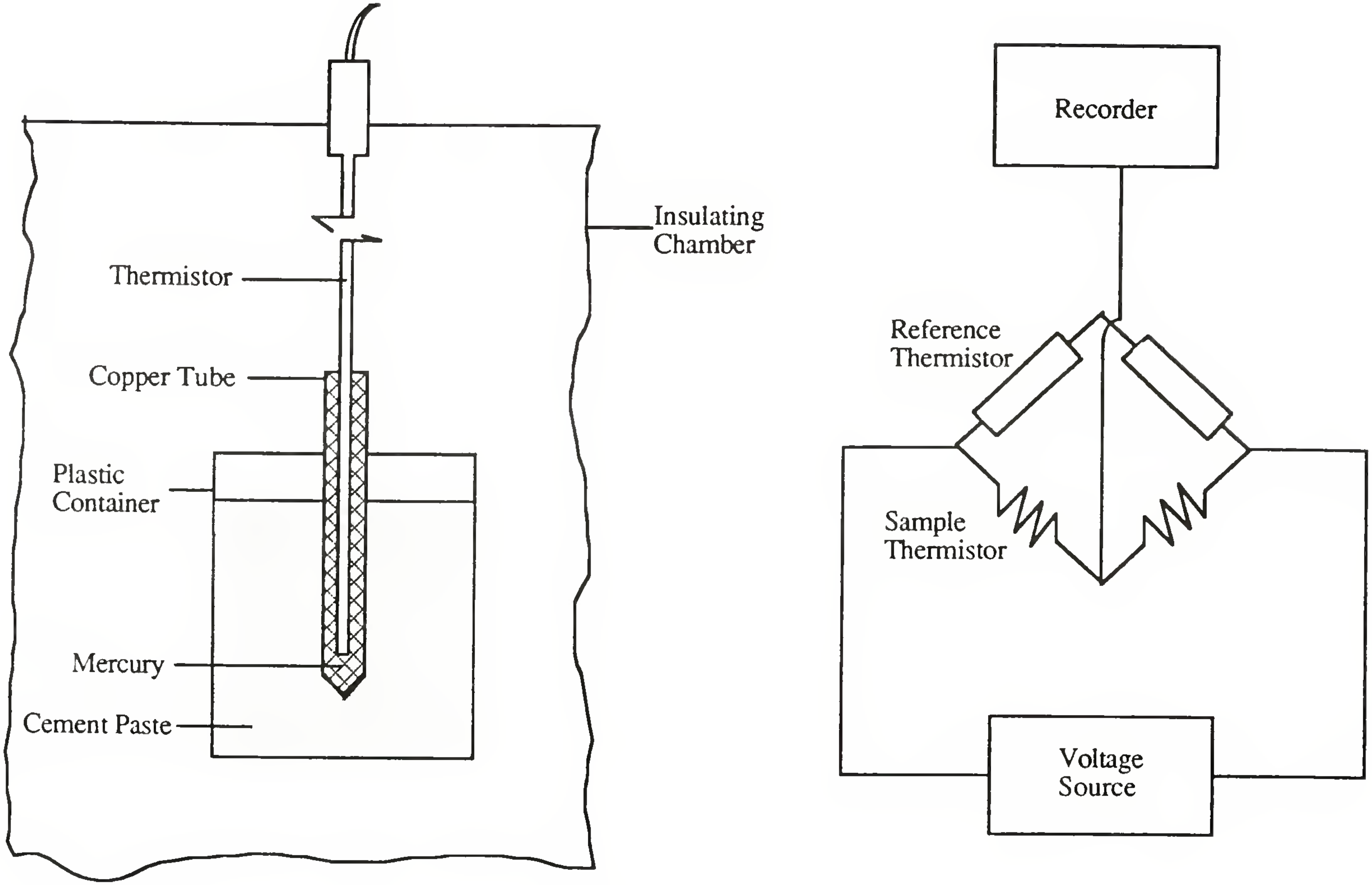

Figure 4.6-1 Schematic view of the apparatus used to measure the temperature evolution.

the thermistors. The thermistors were then inserted into a copper tubes which were in turn positioned through the openings in the lids. The bottoms of these tubes had been previously crimped shut, and approximately 1 ml of mercury was placed in each tube so as to surround the thermistor and improve heat transfer between thermistor and the wall of the copper tube. The thermistors were than embedded in the paste and reference material and connected to the Wheatstone bridge circuit.

As the hydration reactions increase the temperature of the paste system, the accompanying drop in resistivity of the thermistor is converted into a voltage difference between the two branches of the Wheatstone bridge circuit to which the paste and the reference thermistors were connected. This voltage difference is fed into a strip-chart recorder for a continuous readout. The system was previously calibrated in order to establish the relationship between voltage difference and temperature change. The calibration curve obtained for the set of thermistors and the Wheatstone bridge used in the course of this study is presented in Fig. 4.6-2.

In all case the time needed for transfer of paste from the mixer into the temperature measuring device was kept as short as possible; the actual temperature measurements were able to be started about 5 minutes after the water was added to the cement-fly ash mix.

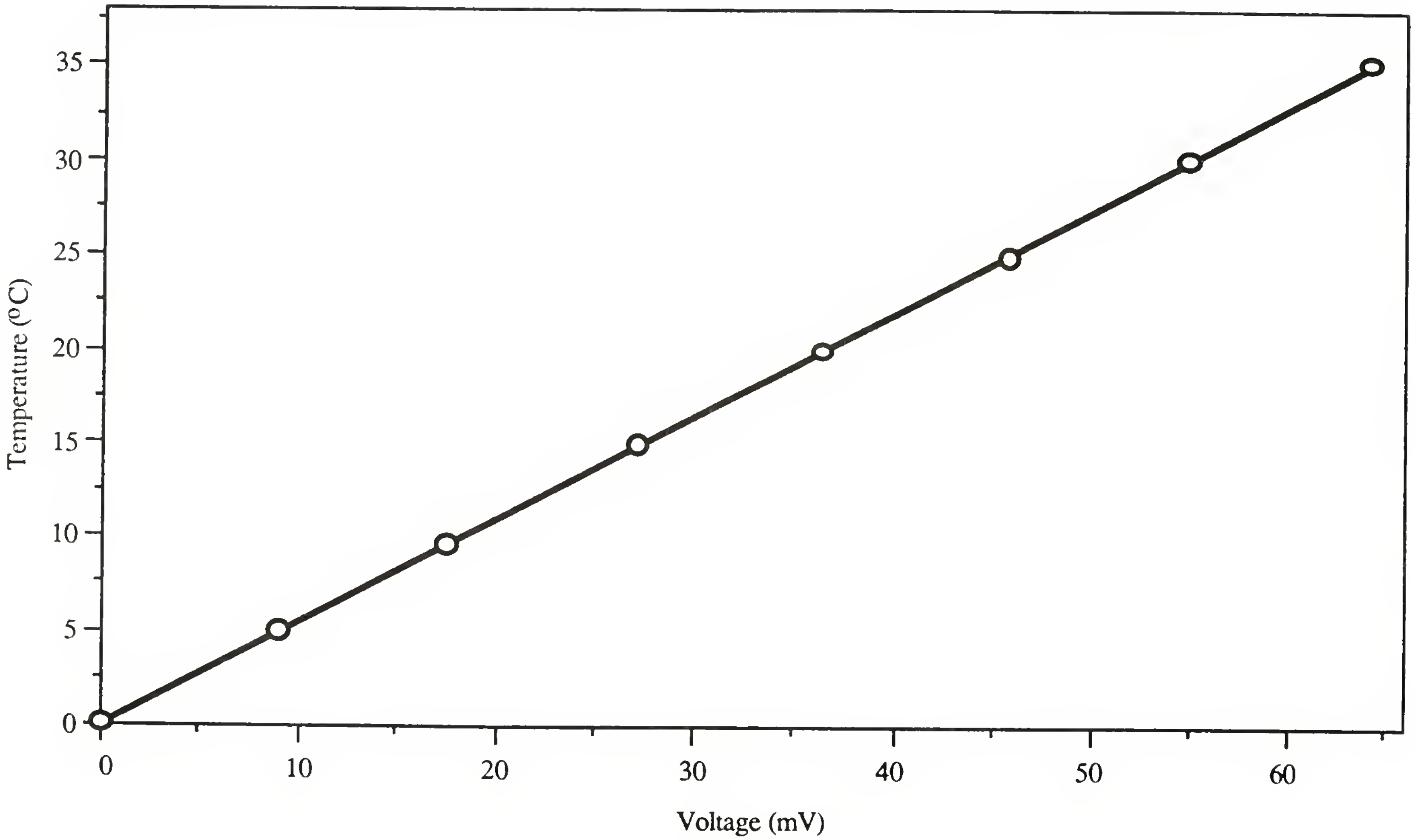

Figure 4.6-2 Calibration curve for temperature evolution test.

4.7 Mixing Procedure and Testing of the Fresh Concrete

The ASTM C 192-76 [209] procedure was followed in making the concrete mixes. A Lancaster pan mixer of 4.0 cu. ft. nominal capacity was used, and the maximum volume of concrete mixed at a given time was about 2.1 cu. ft.

Prior to starting rotation of the mixer, the coarse aggregate and about 1/3 of the mixing water was placed in the pan. The mixer was than started and the sand, cement, fly ash and water were added sequentially. The air entraining admixture was dissolved in the mix water before it was added to the mixer. After all of the ingredients were placed in the pan the concrete was mixed for 3 minutes. This was followed by 3 minutes rest and a 2 minutes period of final mixing.

Immediately after the mixing a slump test was conducted according to ASTM C 143-78 [210]. The unit weight of the concrete was then determined, according to the procedure given in ASTM C 138-77 [211].

The air content of the freshly mixed concrete was then measured using the standard pressure method ASTM C 231-78 [212].

The VeBe time for the concrete was then determined in accordance with the usual procedure as recommended by the manufacturer. No ASTM standard is prescribed for this test.

4.8 Casting and Curing of Concrete Specimens

Three standard 6 x 12 in. compressive strength cylinders and 3 6 x 6 x 21 in. flexure beams were cast from each mix. The concrete was placed inside the steel molds and consolidated using a steel rod.

The placing and consolidating was done according to ASTM C 192-76 [209]. In all, about 150 different individual batches of concrete were made, with a total of about 1100 specimens being cast. Beams measuring 3 x 3 x 6 in. were cast for freeze-thaw testing. Three freeze-thaw test beams were cast for each concrete mix, for a total of 66 beams.

After casting, the specimens were covered with wet burlap and kept in the molds for 24 hrs. They were then demolded and transferred to a fog room, where they were stored until testing time. The freeze-thaw test specimens were stored in lime water for a period of 14 days after demolding, and then were kept in a freezer until the test was started.

4.9 Testing of Hardened Concrete

This section provides a description of each of the various tests performed on hardened concrete.

4.9.1 Compressive Strength

The ASTM C 39 - 72 Standard Method [213] was followed for compressive strength determination. The standard 6 x 12 in. cylinders were capped prior to testing, following the general procedure described in ASTM C 617 - 76 [214]. A commercial sulfur mortar capping compound was used.

The specimens were tested using a Baldwin hydraulic universal testing machine of 60,000 lbs. capacity. The rate of loading was approximately 35 psi/sec.

4.9.2 Flexural Strength

The flexural strength of concrete was determined using 6 x 6 x 21 in. beams, and following the procedure outlined in ASTM C 78-75 [215] (third-point loading). The specimens were turned on their sides with respect to their positions at molding, and tested in the Baldwin hydraulic universal testing machine. The rate of loading was chosen so as to provide for a stress increase in the extreme fiber of the beam about 150 psi/min.

Since the fracture in all of the tested samples was initiated within the middle third of the span length, the modulus of rupture was calculated using the following formula:

$$R = Pl/bd^2$$

where:

R = modulus of rupture, (psi)

P = maximum applied load indicated by the testing machine, (lbf)

l = span length, (in.)

b = average width of specimen, (in.)

d = average depth of specimen, (in.).

In accordance with the standard practice, no correction was made for the gravitational force exerted by the approximately 65-lb weight of the specimens.

4.9.3 Density

The density of concrete was determined using end pieces of the beams from the flexural test, reduced (by splitting in the testing machine) to approximate cubical shape with dimensions of 6 x 6 x 6 in. Three specimens were prepared from each of the concretes tested, and were submerged in water for a period of 48 hours. After that time they were placed in a container submerged in water and weighed. The specimens were then dried to constant weight at a temperature of 110 ± 5°C and weighed.

The density of concrete was than calculated using the following formula:

$$p = A/(A - C)$$

where:

p = density of concrete, in grams per cubic centimeter

A = weight of oven-dry specimen in air, g

C = weight of saturated specimen in water, g.

4.9.4 Static Modulus of Elasticity and Poisson's Ratio

The values of static modulus of elasticity and Poisson's ratio were determined following the procedure outlined in the ASTM C 469 Standard Test Method [216].

The measurements were performed on standard 6 x 12 in. concrete cylinders prepared in accordance with the procedures described in sections 4.7 and 4.8. Prior to testing the specimens were moist cured for a period of time ranging from 2 days up to 6 months. Such variation of the curing time was used to assure the production of concrete with strength values varying from about 2000 psi to over 6000 psi. This approach was necessitated by the fact that Poisson's ratio values resulting from this limited-scale test were used in calculating the dynamic modulus of elasticity values for concretes with similar strength ranges.

In the present study, both longitudinal and transverse strains were measured with an electrical resistance strain gage (Type EA-06-20CBW-120 manufactured by Micro-Measurements Co., Raleigh, N.C.). These are constantan foil gages with a tough flexible polyimide backing recommended for use on concrete surfaces. The effective length of the gage was 2.0 in., that is, almost 3 times larger than the maximum size of coarse aggregate used in the concrete (0.75 in.).

In preparation for gage installation, the surface of the specimen was abraded with a wire brush and pre-coated with Micro-Measurement M-Bond EA-10/15 epoxy resin. The epoxy resin was worked into existing surface pores and then leveled to form a smooth surface. When the epoxy resin hardened, it was abraded again until the base concrete begin to be exposed. Following this the gage area was degreased (using Freon spray) and then abraded with No. 320-grade abrasive paper. The surface of the sample was then marked with a pair of crossed reference lines and neutralized with Micro-Measurements Neutralizer 5. The gages were than installed (using M-Bond AE-10/15 epoxy resin) so that the triangular index marks defining the longitudinal and transverse axes of the grid were aligned with the proper reference line.

Two of the gages were centered about mid-height of each cylinder on diametrically opposite sides, and were positioned parallel to the axis of the specimen. These gages were used to monitor the longitudinal strains, which were used in calculating the modulus of elasticity values. A second pair of gages, used for measuring the transverse strains (for Poisson's ratio determination), was also mounted circumferentially at diametrically opposite points at the mid-height of the specimen. The end faces of the cylinder were then capped following the standard ASTM C 617 procedure [214].

Before the modulus of elasticity and Poisson's ratio testing were performed, three cylinders of the same age and type were tested in compression in order to establish the value of the ultimate load.

The specimen to be tested was placed on the lower platen of a 120,000 lb. capacity Baldwin universal testing machine, and had its axis carefully aligned with the center of the spherically-seated upper bearing block. The leads of the strain gages were then connected to the data acquisition system, which automatically recorded the strain values simultaneously from all four gages, at a rate of about 80 entries per minute. The load corresponding to a given strain was recorded in the same fashion, using the feedback signal from the properly calibrated LVDT mounted on the testing machine as an indicator of force applied to the specimen.

Following the current standard ASTM procedure, before recording the strains, the specimens were pre-loaded to about 40 percent of the ultimate strength at a constant rate of loading 35 psi/s. The load was then released at the same rate. No readings were recorded during this first run, which served mainly to seat the strain gages and correct the sample eccentricity. The strains were then recorded during a second run, in which the specimens were loaded to the same level and at the same rate as during the initial loading. Two specimens were tested for each strength level considered.

4.9.5 Dynamic Modulus of Elasticity

Values of the dynamic modulus of elasticity were determined using the pulse velocity method. The measurements were performed on 6 x 6 x 21 in. beams at ages 1, 3, 7, 28, 90 and 180 days.

The instrument used in this measurements was a portable V-meter Model C-4901, manufactured by James Instruments Inc. It generates low frequency ultrasonic pulses, and measures the time taken for them to pass from one transducer to the other through the material interposed between them. The instrument has a digital display which gives a direct reading of the pulse transition time. The measurements were made with 54 kHz frequency transducers, and the time readings were considered accurate to 0.1 μsec. An instrument zero was checked prior to each actual measurement using the standard reference bar supplied with the apparatus. The pulse transit time for the bar was 26 μsec.

The transmitting and receiving transducers were placed in contact with the opposite ends of the sample being tested thus providing for direct transmission of pulses through a distance of 21 in. The exact distance between the transducers was carefully measured for each sample and this number was used when calculating the velocity values. In order to assure proper coupling, a water pump grease was applied to each of the transducer faces before placing them in contact with the specimen surface. The transducers were than pressed hard against the ends of the concrete beams and held continuously against them until a consistent reading appeared on the display. When the units digit repeatedly oscillated between two values the mean value of the display reading was taken as a data point.

4.9.6 Freeze-Thaw Resistance

The determination of freeze-thaw resistance of concrete samples was performed by Materials and Test Division of the Indiana Department of Highways at their test facility located in Indianapolis.

The concretes used for freezing and thawing test were taken from the same batches as that used for strength specimens. The mix proportions are summarized in Table 5.4-1. Table 6.5-1 gives the results of an air content determinations on the fresh concrete, carried out in accordance with ASTM C 231 method [212]. Upon mixing the concrete was placed in 3x3x15 in. beam steel molds, and cured in the laboratory environment for a period of 24 hours. The specimens were than demolded and placed in saturated lime water, where they remained for an additional 13 days.

Three specimens were produced and tested for each of the twenty two types of concrete tested, providing a total of 66 tested specimens. The specimens were carefully weighed just prior to being placed into the testing cabinet, and readings of the initial value of resonant frequency were taken.

The freeze-thaw equipment used exposed the specimens to 12 cycles per day of rapid freezing in air and thawing in water, in accordance with ASTM C 666 procedure B [4]. The equipment was a Conrad device which handled all 66 specimens at the same time. The specimens were oriented vertically and were rotated 180° at the time of each frequency reading.

The frequency readings were carried out at intervals of approximately every 30 cycles, at the end of a thaw cycle. Since there was no indication of early sample failure, the tests were continued until the ASTM C 666 recommended number of 300 cycles was reached. At the end of the testing program the samples were weighed again in order to determine weight losses.

4.9.7 Chloride Permeability

The chloride permeability of concrete specimens was measured according to the procedure outlined in the "Interim Method of Test for Rapid Determination of the Chloride Permeability of Concrete, AASHTO Designation T 277-83I" [217].

The procedure above was developed to determine the chloride permeability of concrete in existing structures. The results of the test are evaluated using the presumed relationship between the chloride permeability and electrical conductance, i.e. the charge (coulombs) passed as given in Table 1 of AASHTO T 277-83I. This table is reproduced below as Table 4.9-1.

Table 4.9-1 Chloride permeability based on the charge passed [3].

Charge Passed Typical of	Chloride (coulombs)	Permeability
>4.000	High	High water-cement ratio, conventional (≥0.6) PCC
2.000-4.000	Moderate	Moderate water-cement ratio, conventional (0.4-0.5) PCC
1.000-2.000	Low	Low water-cement ratio, conventional (<0.4) PCC
100-1.000	Very Low	Latex-modified concrete Internally sealed concrete
<100	Negligible	Polymer impregnated concrete Polymer concrete

The values in Table 4.9-1 were developed from data on 3.75-in. diameter x 2.0-in. long core slices; no relationships have yet been established which would allow their adjustments for data obtained from other types of specimens. Accordingly, in order to prepare a test specimen in accordance with the specification, a 3.75 in.- diameter core must be obtained from the structure using a core drilling rig. Upon obtaining the core, a 2 in.- thick slice is then cut from the core and used as a test sample.

In the present study, specimens of the same 3.75 in. diameter required by AASHTO T277-83I were used, but they were cast in molds rather than being drilled from a larger structure. Since 3.75 in. diameter cylindrical molds are not readily available, the molds used in this investigation were specially made, using standard PVC sewer pipe. The pipe internal diameter of 3.75 in. ideally matched the desired specimen diameter; its 1/8 in.- thick wall was sturdy enough to support the pressure of the fresh concrete without buckling.

A 12 in.- long section of the pipe was used as the mold. Such long cylinders were selected in order to reduce the influence of casting procedure on the quality of test sample, and to increase the number of samples from the same batch.

The 12 in.- long mold was positioned vertically on a glass plate and the fresh concrete (mixed according to the procedure described in section 4.7) was placed within it in three approximately equal layers. Each layer was compacted by rodding, using 25 strokes of a 3/8 in. diameter steel rod. The open surface was covered with wet burlap to prevent evaporation.

Concrete cylinders prepared in this manner were stored for 24 hours in the laboratory environment. At the end of 24 hour period, the molds were split open, and the sample cylinders were transferred to a moist curing room where they were stored for additional six months.

After six months of moist curing, 2 in.- thick slices were cut from the top and the bottom of each cylinder. These slices were used as the test specimens in the chloride permeability test.

Following the cutting operation each of the slices was allowed to surface dry for one hour. The samples were than placed on a support stud, and their sides were coated with rapid setting epoxy (CIBA brand GY-6010 resin and HY-9225 hardener mixed at 1:1 by weight).

The samples were then vacuum saturated for 18 hours with previously boiled deionized water, in order to assure their complete saturation. This step is very important in sample preparation as the degree of saturation has direct impact on the conductivity values obtained. Samples prepared in the above manner were than mounted in the test cell.

The test cell was composed of two 6x6x2 in. acrylic plates, each provided with a compartment to hold a solution used during testing, and with a copper screen which served as an electrode. The sample was positioned between the plates of a test cell and its flat surfaces were pressed against the copper screens. The specimen - cell boundary was than sealed, using Rutland brand RTV silicon sealant in order to assure that there would be no leakage of solution during the test.

One of the test cell compartments was than filled with sodium chloride solution (3% by weight of reagent grade NaCl), and its copper screen was connected to the negative pole of the measuring instrument. The specimens were always positioned so that the molded surface of each specimen was always placed facing the negative side of the cell. The other compartment, connected to the positive pole of the measuring instrument, was filled with 0.3 N sodium hydroxide (reagent grade) solution.

The test involved subjecting the test cell to a 60 volt DC potential. This potential forces the migration of ions towards the electrode of opposite sign and the resulting current flow is recorded over a six hour span. The current flow is than integrated over time to provide a total coulomb figure for the six hour test. This is the standardized parameter relatable to chloride permeability.

In these experiments, the measurements and the integration of current and time were done automatically, using a Model 159 Test Set produced by RLC Instrument Co., Akron, Ohio. This particular instrument is only capable of measuring one sample at a time, although others that do several samples simultaneously are available. It generates a printout of time, current and coulombs at 30 minute intervals, and automatically terminates the test at the end of a six-hour period.

After the test was terminated, the 6 hour coulomb value recorded was referred to the Table 4.9-1 reprinted from AASHTO T 277-83I in order to assess the relative chloride permeability of a given sample.

5.0 THE DEVELOPMENT OF THE "CPQ" MIX DESIGN METHOD FOR FLY ASH CONCRETES

This chapter describes the series of preliminary experiments which led to the development of a new fly ash concrete mix proportioning method. This method attempts to provide for a constant quality of cement paste in fly ash concrete, regardless of variations in the source and properties of the fly ash used; in the discussion that follows it will be referred to as the "Constant Paste Quality" or CPQ mix design procedure.

5.1 Introduction

The review of existing fly ash concrete mix proportioning methods presented previously reveals that most of them do not consider all of the important properties of concrete relevant to a particular application. Rather, the focus is ordinarily on achieving a given level of compressive strength in an economical manner with the job materials available. Usually this strength requirement is based on the expected behavior of plain concrete with portland cement alone.

Due to the variations to be expected in the properties of different fly ashes, such mix design procedures can not provide reasonable assurance that fly ash concrete designed to meet a given compressive strength level will perform satisfactorily in other respects. Such an expectation is reasonable for plain concrete. However, for fly ash concretes batched with variable sources of fly ash the strength criterion alone is inadequate as a guide to proper mix design.

A major reason for this is that variation in fly ash properties can result in variations in fly ash-cement paste quality that may seriously affect the performance of the concrete. Durability characteristics, in particular, may be adversely impacted.

There is no single parameter or group of parameters that unambiguously defines the effect of a particular fly ash on the behavior of the fresh concrete mix, or on the resulting strength and durability characteristics of the hardened concrete. It is evident to those with relevant experience that the standard pozzolanic activity index test is inadequate for this purpose. Lacking such an index, optimization of a concrete mix design with fly ash is rarely attained.

The purpose of this part of the study was to develop a new procedure for undertaking the design of concrete mixes with fly ash, to attempt to insure that the resulting concrete product will not only be strong enough for the intended purpose, but will have some assurance of adequate durability characteristics as well.

The mix design procedure developed is an adaptation of a method originally suggested by Cordon and Thorpe [217] for the design of plain concrete mixes, here extended to cover the more complicated problem of mix design for fly ash concretes.

The method proposed does not concern itself with prevention of specific durability "syndromes" like alkali-aggregate reaction, sulfate attack, or steel corrosion; nor is it specifically pointed at the prevention of freeze-thaw problems. It is assumed at the outset that the concrete materials to be used are such as not to render the concrete unduly susceptible to these specific problems, or if they are, that adequate measures to prevent the problems, such as proper air entrainment, are already part of the mix design process. Rather, the proposed method is aimed at attempting to provide that concrete with a constant and acceptable quality of cement paste is routinely batched, in the face of expected variations in behavioral characteristics of fly ashes from one source or job to another.

It is considered that the general durability of concrete exposed in service is usually limited by high water contents needed to provide easy workability in field placement and easy consolidation. High water contents lead to the production of concrete containing cement paste of variable and badly-controlled quality. The problem may be accentuated when fly ash of indifferent quality is included in the mix, particularly for fly ashes that may increase the water demand. A mix design method is needed that will guard against the possibility of this happening.

5.2 Development of CPQ Fly Ash Concrete Mix Proportioning Method

The proposed procedure is primarily concerned with maintaining the quality of paste in fly ash concretes.

It is ordinarily assumed that as long as the portland cement itself is satisfactory, the quality of the cement paste produced in plain portland cement concrete is primarily an inverse function of the water:cement (w:c) ratio.

On introducing fly ash into the mix, one automatically introduces an important additional variable that influences paste quality and consequently the overall quality of the concrete. It is assumed here specifically that for fly ash - cement paste, the quality is also primarily an inverse function, but now of the water:cementitious solids ratio. The portland cement and fly ash are intimately mixed in the paste, and both may take part in the hydration reaction processes. Both need to be included in calculating the effective water:"cement" ratio, which is here properly the water:(cement + fly ash) ratio. For convenience, the water:(cement plus fly ash) ratio will be referred to as w:(c+fa).

The crux of the mix design method proposed here is that no adjustment of, or change in, the specified w:(c+fa) is permitted in the mix design process at all. Instead of the common practice of adjusting the water content to arrive at a satisfactory level of workability as indicated by a specified slump, in the proposed method the slump is adjusted by keeping the paste composition constant, but increasing or decreasing the proportion of aggregate to paste until the required slump is attained.

It is recognized that this feature may sometimes reduce the economy of the mix, since with some fly ashes a reduction of the amount of aggregate and therefore an increase in the amount of cement may be necessary. However, at least as far as paste quality can be specified in terms of a constant w:(c+fa) ratio, and durability can be specified by an appropriate level of paste quality, this will be assured regardless of the effects of the particular fly ash used.

The major steps in the proposed mix design procedure are outlined in Figure 5.2-1.

The design procedure starts with setting the basic requirements for the concrete, as determined by particular construction and service demands. In addition to the all-important specified constraint on w:(c+fa), such requirements can include criteria for minimum acceptable compressive strength at specified ages, minimum cement contents, slump criteria, air content specifications, requirements for maximum size of the aggregate, specification of portland cement type if a specific type is needed for a particular job, specification of a class or specific source of the fly ash, and decisions relating to type and quantity of any chemical admixture to be used. Constraints on all of these can be accommodated in the methods.

After establishing the initial set of assumptions and constraints and obtaining the candidate materials, one next has to decide on the w:(c+fa) ratio that will provide appropriate assurance of satisfactory paste quality for the particular concrete concerned. Even if records indicating the performance of concrete with the particular fly ash are not available, one can start with a w:c value that would be recommended for plain concrete in a similar service environment.

However, one should be aware that at any given w:(c+fa) level, the early age strength developed with certain fly ashes may be less than that expected with the same w:c ratio in plain concrete.

The next item to be decided upon at this initial stage of design is the percentage of the fly ash to be used. Depending on the charac-

MIX DESIGN PROCEDURE

1. Set the basic requirements for the plain concrete mix.
2. Select the replacement level of fly ash desired.
3. Select the "under-replacement" factor desired.
4. Select the proportions of coarse aggregate and sand to be used.
5. Establish the mix proportions for a given workability.
6. Prepare a trial batch (measure unit weight, calculate yield).

Figure 5.2-1 The major steps of the CPQ mix design procedure.

teristics of the individual fly ash, the job requirements, and the properties of the other ingredients, fly ash contents ranging from 15 to 25 percent by weight of cement are usually recommended; higher contents can often be used if desired.

Next, the cement content is suitably adjusted to take advantage of the potential for economy provided by the fly ash. It is ordinarily recommended that this reduction in cement content be no more than 80 percent of the weight of the fly ash to be incorporated, so as to maintain early age strength development in the fly ash concrete at about the level expected with plain concrete.

After the above decisions have been made, a series of at least three trial batches are mixed. A standard convenient paste batch size is decided on, and each mix should consist of an identical batch of paste of the specified constant w:(c+fa) ratio, to which a measured amount of saturated surface dry aggregate has been added.

Before producing the trial batches a decision is required regarding the proportion of coarse aggregate to sand to be used in the trial mixes. The proposed mix design method does not require that any specific criterion be used to select this proportion. In the present work, the proportion which resulted in maximum bulk density of the combined aggregate was used, but this does not have to be so. For the coarse aggregate and sand used in this project, these proportions turned out to be 46% sand and 54% of the crushed limestone coarse aggregate by weight.

The amount of combined aggregate to be added to the paste batch in the first trial mix should be such that it produces a slump somewhat higher than is to be used in practice. In the preliminary trials for this research, the amount added was only enough to produce concrete of slump within a broad range of 5 to 7 inches, much higher than the target value of 3 inch slump chosen for the final concrete.

For the second trial batch, a substantially greater amount of aggregate is added, so as to produce concrete of slump lower than desired in the final mix. In the preliminary trials the aim was to produce concretes with slumps on the order of 1 to 2 inches.

The unit weight and percent of air was measured for each of the batches, and strength specimens were cast for testing at required ages.

The next step in the process is to prepare a chart of slump vs. batch aggregate content similar to that shown in Figure 5.2-2. From this chart the amount of aggregate needed to produce any desired intermediate slump can be estimated. The experience gained during these preliminary studies indicated that the relationship between the slump and the aggregate content is almost always sufficiently linear so that only the two end member mixes actually need to be produced to define the behavior of the system.

At this point a third "record" trial batch is produced, using the aggregate content selected from the chart that presumably will produce concrete of the slump desired for the final mix, and the fact that the desired slump is actually generated is confirmed. If this confirmation is obtained, the air content, unit weight, and strength of this "record" batch are evaluated. If these parameters satisfy the specified requirements for the concrete mix, the mix proportions of the

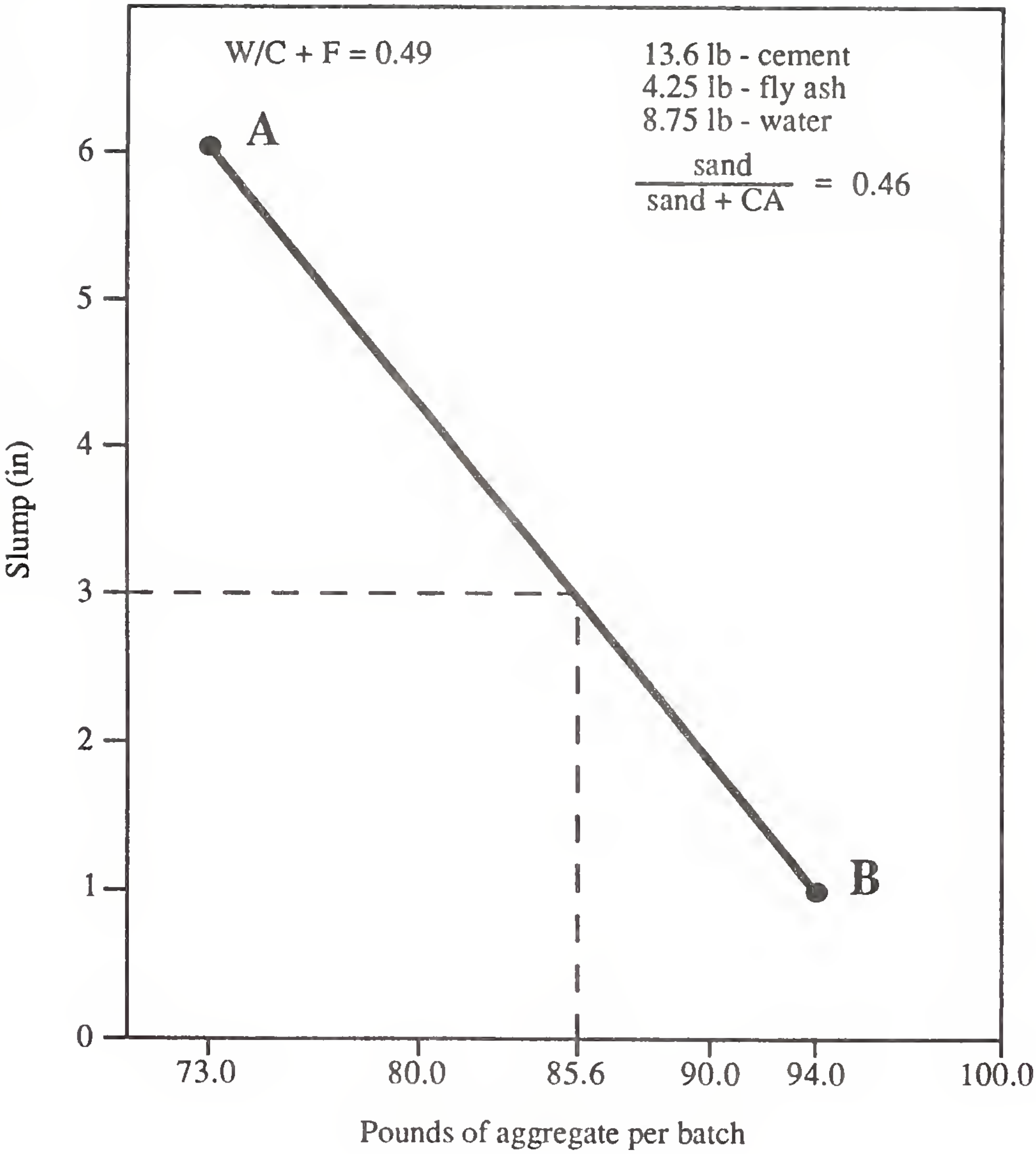

Figure 5.2-2 Slump variations as a function of aggregate content of the batch.

third trial batch can be regarded as a basis for full scale mixes.

To illustrate the process of arriving at the final full scale mix design on a cubic yard basis, a set of actual calculations are provided in the numerical example below.

It was assumed in these calculations that a fly ash concrete needs to be produced that for reasons of economy just satisfies the requirements of the Indiana Department of Highways specification for portland cement concrete pavement [196, Sect. 501)].

The maximum water:cement ratio allowed in this specification is 5.5 gallons of water per sack (94 lb.) of cement used, which is equivalent to w:c = 0.49. The design process was started with arbitrarily selected value of 17 lb. of cement as the basis for the batch. Assuming that the desired fly ash "replacement" level is 25% of the cement basis used, one will need to use 17 x 0.25 = 4.25 lb. of fly ash in each trial batch.

As discussed earlier, it is often considered undesirable to remove more portland cement than 80% by weight of the fly ash to be used. Accordingly, only 80 percent of that value or 0.8 x 4.25 = 3.40 lb. of cement is removed from the original 17 lb. basis.

The initial values of the solid paste components are thus:

C = 17 - 3.4 = 13.6 lb.

FA = 4.25 lb.

Total 17.85 lb.

The amount of water required is then calculated from the previously established w:c ratio of 0.49.

W = 0.49 x 17.85 = 8.75 lb.

When 73.0 lb. of saturated surface dry aggregate (46 percent sand, 54 percent coarse aggregate by weight) was added to a paste batch as specified above, concrete with a 6.0 in. slump was obtained. This result was plotted as point A in Figure 5.2-2. A second identical paste batch mixed with 94.0 lb. of combined aggregate yielded concrete of 1.0 in. slump. This was plotted as point B in the figure.

It is evident from Figure 5.2-2 that to obtain concrete with the desired 3.0 inch slump, a paste batch with about 85.6 lbs. of combined aggregate should be used.

When a mix containing that amount of aggregate was produced it yielded a satisfactory slump of 3.25 in. The unit weight of the mix obtained was 3907 lb./cu yd., and the air content and strength development were satisfactory. Thus, the third trial batch was regarded as a satisfactory basis for full scale trial mixes.

A procedure for converting the mix proportions from pounds per batch to pounds per cubic yard is demonstrated below.

Proportions of the Trial Batch

Material	Amounts (lb.)
cement	13.60
fly ash	4.25
water	8.75
aggregate	85.60
Total	112.20

Yield: Batches/cu yd.

3907/112.2 = 34.82

Mix Proportions:	lb./cu yd.
cement	13.6 x 34.82 = 473
fly ash	4.25 x 34.82 = 148
water	8.75 x 34.82 = 305
aggregate	85.6 x 34.82 = 2981
Total	3907

Aggregate:

Sand	46 percent of 2981 = 1371 lb.
Coarse Aggregate	54 percent of 2981 = 1610 lb.

5.3 Summary of the Preliminary Studies

The mix design procedure described in section 5.2 was followed in preparing a number of a small size (≈ 0.7 cu. ft.) concrete mixes using cement L and fly ashes F1, F2 and C2 at a 25% replacement level. One of the goals of these initial investigations was to see if the suggested design procedure would work with a range of fly ashes of varying properties; the other was to check whether the proposed procedure does in fact yield fly ash concrete whose properties are comparable in both fresh and hardened states with those of the equivalent plain portland cement concrete.

In this preliminary investigation, only such properties as slump, air content, unit weight and compressive strength at 1, 3, 7 and 28 days were tested. In general, the results indicated that the fly ash concretes designed using this CPQ method attain similar characteristics to those attained by the reference plain concrete. In addition, the proposed method was found to be sensitive to the variations in the fly ash properties and permitted easy adjustments of mix proportions where necessary.

In summary, the results of the preliminary investigations were encouraging enough, that the CPQ method was used to design all of the concrete mixes required in this research program.

6.0 DESIGN OF FLY ASH CONCRETE MIXES USED IN THIS STUDY AND NOTES ON WORKABILITY AND ECONOMY

6.1 Design and Coding of Concrete Mixes

The concrete mixes used in this study were all designed using the CPQ method outlined in the preceding chapter and batched using the materials described previously. The specific combinations of materials included the single coarse aggregate and sand, and all combinations of the two cements and the five fly ashes described.

Two replacement levels, described for simplicity as 15% and 25% replacements by weight were used to produce the test concretes.

Since direct weight-for-weight substitution of fly ash for portland cement usually leads to reduction of early age strength, the cement content in each case was reduced only by 80 percent of the weight of the fly ash added to a given mix. In other words, for every 100 lbs. of fly ash added only 80 lbs. of cement was removed from the mix.

The two levels of replacement, in combination with the two types of cement, and the five types of fly ash gave rise to 20 different mixes. In addition two reference mixes were also produced using cement alone, bringing the total number of different mixes to 22.

In order to be able to easily identify these various mixes, the following coding system was implemented:

(1) The plain concrete mixes were coded by a single letter (L or S) indicating the brand of cement used, as described in Section 3.2

(2) The mixes containing fly ash were coded using a three-part description, for example LC1(25). The first part of that description indicates the brand of cement used in the mix, in this case cement L. The second part indicates the fly ash used, in this case fly ash C1. The third part indicates the replacement level, in this case 25%.

The symbols used to distinguish between the different fly ashes were assigned in Section 3.1, and their properties summarized in Tables 3.1-1 to 3.1-3.

The actual mix compositions of all of the 22 mixes used in this study are given on a per cu yd. basis in Table 6.1-1.

The entries in this table have an unusual significance, in that they represent not the theoretical batch design (as is usually the case) but the true average composition per unit volume, of all of the concrete produced for that mix. In this research the volume of experimental concrete required for all of the testing performed was approximately 12 cu ft. The optimum batch size for the mixer used is approximately 2 cu ft. Thus a total of six individual batches of each mix had to be prepared. Each individual batch was tested for yield, and the individual compositions (for a cubic yard basis) recalculated.

The data for each mix given in Table 5.4-1 represent the average of such calculations for the six batches of each mix.

The composition of each batch was based on the design composition required for a 3 in. slump, as determined using the procedure

Table 6.1-1 Composition of mixes used in this study.

Mix	Materials (lbs./cu yd.)						
	Cement	Fly Ash	Total (C+F)	Water	Sand	Coarse Aggreg.	Total Aggreg.
L	610	--	610	300	1338	1569	2907
LF1(15)	469	84	553	269	1370	1608	2978
LF2(15)	496	86	582	285	1342	1565	2907
LF3(15)	493	86	579	283	1377	1604	2981
LC1(15)	444	78	522	256	1414	1654	3068
LC2(15)	476	82	558	275	1382	1613	2977
LF1(25)	456	141	597	293	1323	1540	2863
LF2(25)	440	137	577	282	1354	1574	2927
LF3(25)	437	137	574	281	1349	1569	2918
LC1(25)	430	135	565	276	1369	1597	2966
LC2(25)	412	129	541	265	1386	1621	3007
S	610	--	610	299	1341	1571	2912
SF1(15)	480	83	563	276	1354	1581	2935
SF2(15)	500	87	587	288	1350	1572	2922
SF3(15)	490	84	574	281	1369	1578	2947
SC1(15)	456	79	535	262	1398	1630	3028
SC2(15)	479	83	562	276	1380	1613	2993
SF1(25)	456	141	597	293	1323	1541	2864
SF2(25)	430	134	564	276	1361	1586	2947
SF3(25)	430	134	564	276	1362	1586	2948
SC1(25)	444	139	583	285	1352	1574	2926
SC2(25)	411	129	540	265	1384	1620	3004

described in Section 5.2, i.e. scaling off the amount of aggregate from a graph similar to that presented in Figure 5.2-2.

6.2 The Effect of Aggregate Content on the Slump and Workability of the Fresh Mixes Containing Fly Ash.

It is instructive to examine the effects of the different fly ashes on the aggregate contents required to maintain the constant 3 inch slump specified at the beginning of the design process. This required aggregate content might be called "aggregate demand" by analogy with the conventional concept of water demand in ordinary terminology.

The results of all of the mix trials are shown in Figures 6.2-1 and 6.2-2, plotting in each case slump vs. the weight of aggregate added to each standard cement paste batch. In each case, as mentioned previously, slump is inversely related to weight of aggregate added to the standard cement paste batch, the relation being always linear.

The analysis of Figures 6.2-1 and 6.2-2 shows that the slopes of the linear relationships are all negative and fall into two different groups, depending on the fly ash, cement, and replacement level used in a given mix.

The first group could be called a "low slope" group, and includes the reference mixes with both cement "L" and cement "S", and several of the fly ash mixes. With cement L, these include mixes containing fly ashes F1, F2 and C1 at the 25% replacement level, and fly ashes F2 and F3 at the 15% replacement level. For mixes prepared with cement

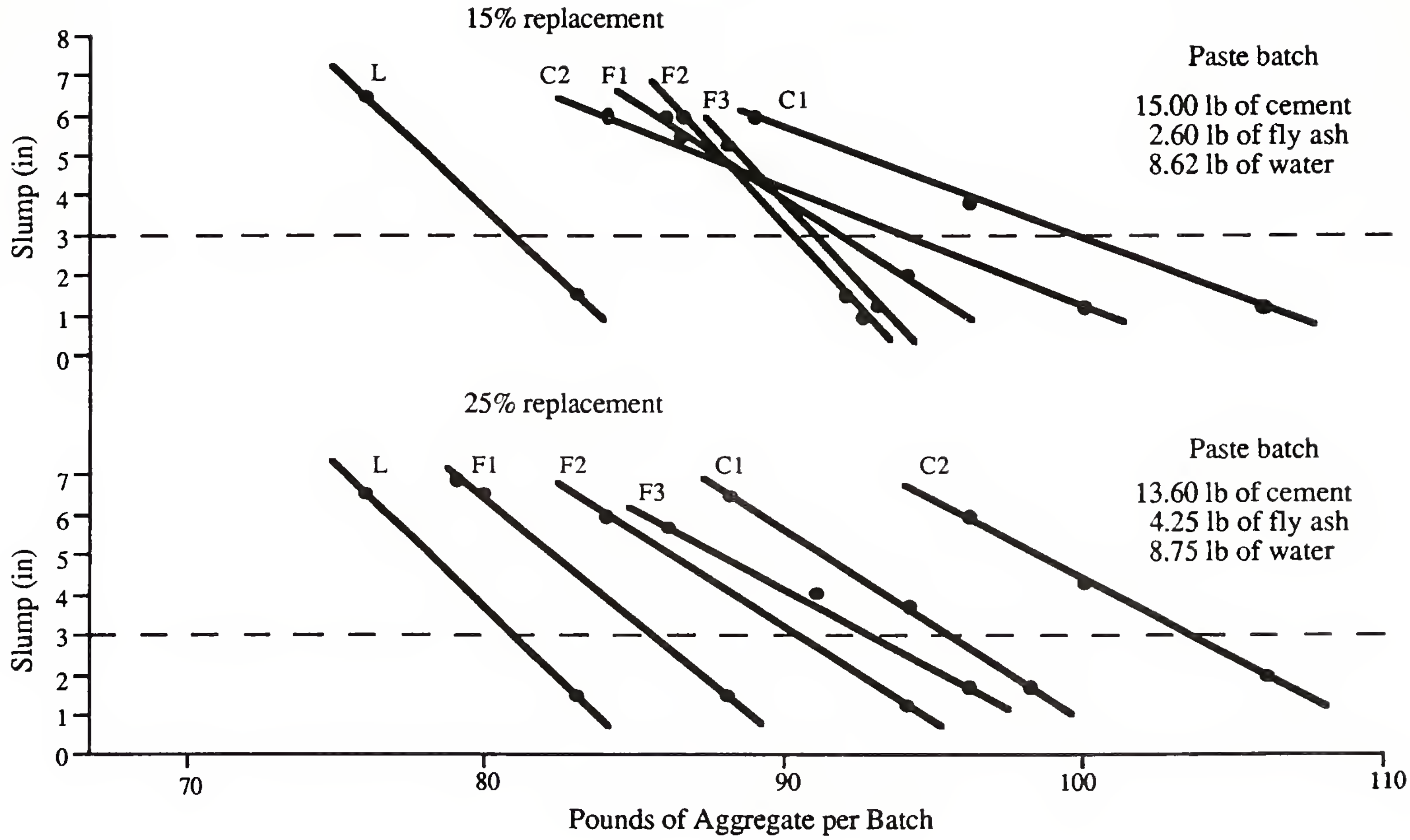

Figure 6.2-1 Slump variations as a function of aggregate content and type of fly ash used, (cement "L" mixes).

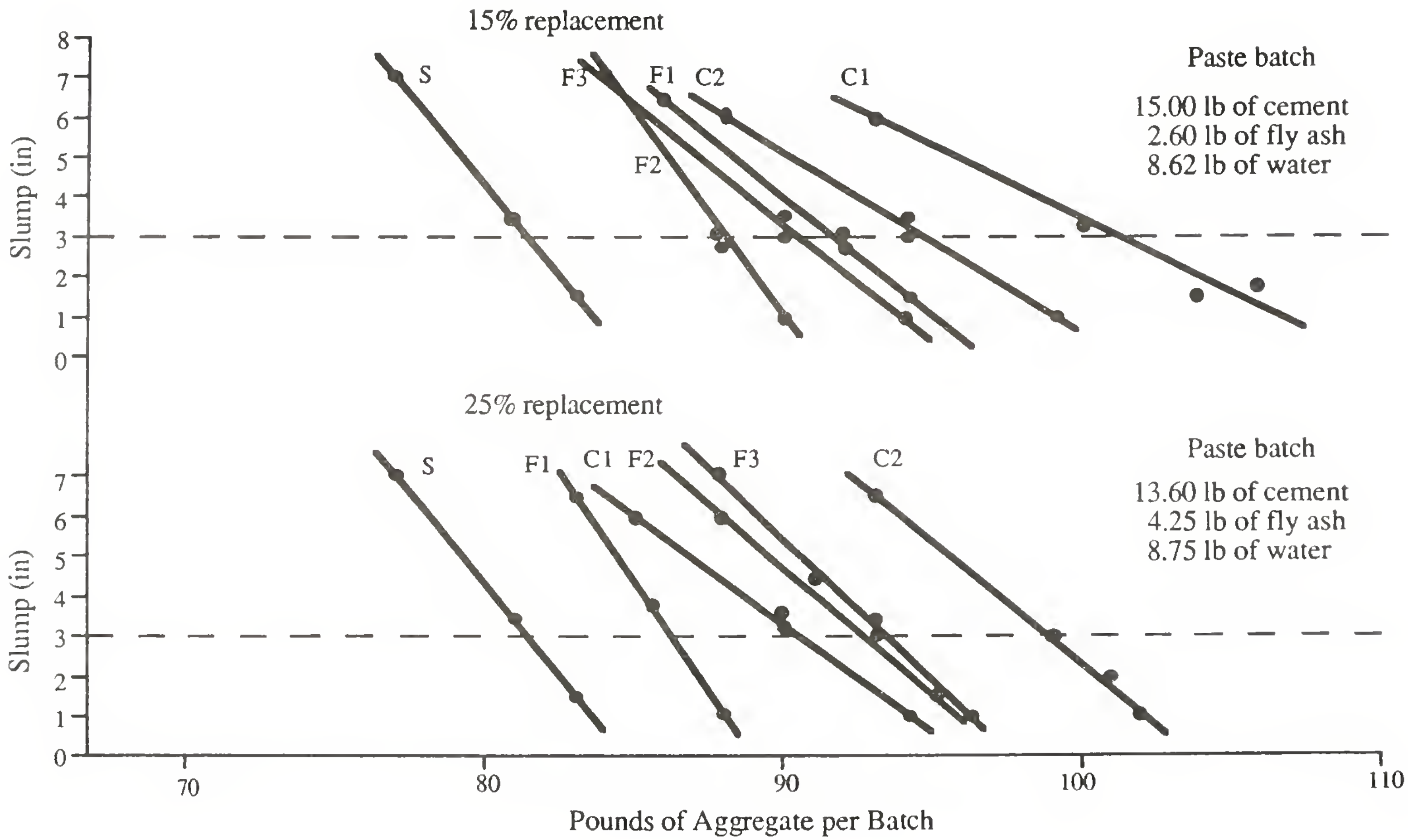

Figure 6.2-2 Slump variations as a function of aggregate content and type of a fly ash used, (cement "S" mixes).

S, the "low slope" group includes fly ashes F1 and F3 at the 25% replacement level, and fly ashes F1, F2 and F3 at the 15% replacement level.

The second group is a "high slope" group, which for concrete batched with cement L includes mixes with F3 and C2 ashes at 25% replacement, and C1 and C2 ashes at 15% replacement. For cement S - based concretes the high slope group includes mixes with C1 and C2 ashes at both replacement levels.

The physical significance of the slope is simply that the higher the (negative) slope, the greater is the incremental amount of aggregate needed to reduce the slump by any specified amount. High slopes, that is, the need for large increments of aggregate to reduce the slump a given amount, were characteristic for all mixes prepared with either of two high calcium fly ashes used in this investigations.

In general all but one of the mixes prepared with cement L showed slightly more negative slope than the corresponding mixes with cement S, which indicates that overall better workability can be expected with cement L.

Of equal significance is the displacement of the line representing the mixes for any specific fly ash concrete from those of the reference plain concrete mix at a given slump level, from left to right on the charts. This displacement can be looked on as a general measure of aggregate demand, or "aggregate acceptance capacity", for a given fly ash paste as compared to the reference plain portland cement paste. The magnitude of this displacement reflects the improvement in concrete workability conferred by the fly ash at the slump and fly ash replacement level used for the comparison. In other words, at a given slump the mixes for which a line representing the relationship between the slump and weight of aggregate in a batch exhibits a larger displacement will have accommodated a higher aggregate content. It was found that such "large displacement" mixes were less sensitive to variations in the aggregate content, and could accommodate such variations more easily, i.e. without excessive slump reduction.

To illustrate the relationships, the displacements exhibited at the 3-inch slump level chosen originally as that desired for the final concrete mixes will be discussed.

In every plot of Figures 6.2-1 and 6.2-2, all of the fly ash mixes are displaced to the right of the portland cement mixes, confirming the increased workability conferred by all of the ashes used.

The 25% replacement plot lines are more readily interpreted, since the lines do not cross each other. It is evident that for 3 inch slump mixes, there is a rank order exhibited by the fly ashes in terms of the amount of aggregate that can be accommodated by the paste batch. Regardless of the type of cement used, the mixes with F1 fly ash are displaced only slightly from those of the corresponding plain cement, that is, mixes with this fly ash accept only a modest additional aggregate increment over that of plain concrete at constant slump. Specifically, in mixes based on cement L, a 3 inch slump for this fly ash requires an 85.6-lb. aggregate batch dosage as compared with an 80.6-lb aggregate batch dosage for the plain portland cement concrete. The corresponding values for concretes based on cement S are 86.2 lbs. and 81.4 lbs. The workability increment associated with fly ash F1 at the 25% replacement level is relatively modest.

At the other extreme, mixes with and fly ash C2 and cement L accommodated 103.4 lbs. of aggregate while maintaining the same 3 inch slump, very much more than the 80.6 lbs. required by cement L by itself. This large difference is a measure of the highly improved workability conferred by using this fly ash at 25% replacement. Corresponding mixes made with C2 fly ash and the other cement, cement S, accommodated 99 lbs. of aggregate at a 3 inch slump. If the strength gain and other properties are satisfactory, it appears that a highly economical concrete can be designed with this fly ash, by taking advantage of the improved workability.

The 15% replacement plot is somewhat more complicated, in that several of the lines cross each other. For concrete made with cement L, the F1, F2 and F3 fly ash lines show similar displacements from the reference portland cement line at the 3 inch slump level, but the F1 line shows a rather steeper slope than the others. The C1 and C2 lines show steep slopes similar to each other, but their order of displacement is reversed from that displayed by these fly ashes at the 25% level. A generally similar pattern is observed for concrete made with cement S, although here the slopes are generally less steep.

It is apparent that the workability effect, i.e. the amount of aggregate that can be incorporated at a given slump level depends generally on the fly ash, but it may be different for the same fly ash used at different percentages, and for different cements. Each base fly ash paste is in fact a separate assemblage of cement particles, fly ash particles, and water, and the characteristics produced are not always simply predictable.

There seems to be a specific effect associated with the replacement level of fly ash used. For all of the fly ashes, the effect of relatively small replacements (15%) is to substantially increase the amount of aggregate that can be added and still retain the same slump. However, if the replacement level is increased to 25%, generally the effect is reduced, rather than increased. Only for one fly ash (C2) when used with one cement (L), could more aggregate be added at 25% replacement than at 15% replacement. This effect appears to limit the potential economic advantage that would otherwise be associated with workability improvement at high fly ash contents.

Finally, a comparison of the graphs in Figures 6.2-1 and 6.2-2 reveals that regardless of the cement type and the replacement percentage used, the two high calcium fly ashes (C1 and C2) produced more pronounced effects on the workability of concrete than did the low calcium fly ashes.

6.3 Final Aggregate Demand and Economic Considerations.

Figures 6.2-1 and 6.2-2, although useful for demonstrating the influence of different fly ashes on the potential mix design parameters, are set up on the original batch weight basis, and do not include any measure of differences in yield of the final concrete mixes.

In order to obtain the yield per cu yd., a conversion procedure such as was shown in the numerical example given in section 5.2.1 must be used. This procedure consists of three basic steps. First, the unit weight of concrete (in lb./cu yd.) has to be measured on a fresh mix sampled from a given batch. Knowing the actual weights of the components used in preparing this batch, one can than calculate the number of batches per cu yd., i.e. the yield expressed in batches, simply by dividing the previously measured unit weight by the total weight of all the components. This calculated yield is then multiplied by the actual weight of each component in the batch to give the weight of that component needed to produce one cu yd. of concrete.

The results of this conversion procedure, averaged for six repeat trials of each concrete, were reported in Table 6.1-1.

In order to simplify the analysis which follows, the weights of aggregate and cementitious materials (cement and fly ash) in 1 cu yd. of concrete were extracted from Table 6.1-1, and reported separately in Tables 6.3-1 and 6.3-2 respectively. To state it unequivocally, these two tables contain the actual average weights per cu yd. of the aggregate and of the cementitious materials needed in mixes corresponding to the 3 inch slump concretes that were diagrammed on a batch weight basis in Figures 6.2-1 and 6.2-2.

The analysis of Table 6.3-1 shows that differences in actual aggregate content (expressed per cubic yard of concrete) between the reference portland cement concrete and the fly ash concretes are not quite as dramatic as might be inferred from Figures 6.2-1 and 6.2-2. The reference concrete has an aggregate content of just over 2900 lbs. per cu yd. At 15% replacement, the fly ash concretes based on cement L average 2.6% more aggregate per cu yd. than this, and these based on cement S only 1.8% more aggregate. At 25% replacement the fly ash concretes average only about 1.0% more aggregate per cu yd. than the plain concrete, regardless of the type of cement.

These values are averages for all the fly ashes. With certain fly ashes at certain levels, for example C1 at 15% replacement, the potential increase in aggregate content per cu yd., of the order of 4% or 5%, might approach economic significance. However, such an effect is clearly not to be generally expected, in that for most combinations the percentage increase in aggregate content is only 2% or less. Thus, it appears that the major economic benefit of fly ash incorporation using CPQ mix design procedure will still stem from the low cost of the fly ash compared to that of the cement it replaces.

This can be seen from the weights of cement and fly ash per cu yd. of concrete as shown in Table 6.3-2. The reference concretes contain 610 lbs./cu yd. of cement. The concretes batched at 15% fly ash replacement average only 476 lbs./cu yd. of cement (for cement L) and 481 lbs./cu yd. of cement (for cement S), and 83 lbs. of fly ash in either case. The mixes batched at 25% replacement average only about 435 lbs./cu yd. of cement, and an average of about 135 lbs./cu yd. of fly ash. On average, for the 15% replacement level, even though we are only removing 12% of the basis cement (80% of the fly ash added) on a batch weight basis, because of changes in yield the effect on a per cu yd. basis is to reduce the needed cement content by about 21%. The analogous reduction for a 25% replacement level is about 28%.

The net economic advantage of these fly ash concretes over the reference concrete naturally depends on the specific local cost of

Table 6.3-1 Total amount of aggregate in 1 cu yd. of concrete.

Mix	Total Aggregate Content (lbs./ cu yd.)	Increase Over the Plain Concrete (%)
L	2907	---
LF1(15)	2978	2.4
LF2(15)	2907	0.0
LF3(15)	2981	2.5
LC1(15)	3068	5.5
LC2(15)	2977	2.4
	Average	2.6
LF1(25)	2863	-1.5
LF2(25)	2927	0.7
LF3(25)	2918	0.4
LC1(25)	2966	2.0
LC2(25)	3007	3.4
	Average	1.0
S	2912	---
SF1(15)	2953	0.8
SF2(15)	2922	0.3
SF3(15)	2947	1.2
SC1(15)	3028	4.0
SC2(15)	2993	2.8
	Average	1.8
SF1(25)	2864	-1.6
SF2(25)	2947	1.2
SF3(25)	2948	1.2
SC1(25)	2926	0.5
SC2(25)	3004	3.2
	Average	0.9

Table 6.3-2 Total amount of cementitious material in 1 cu yd. of concrete.

Mix	Total Amount of Cementitious Material (lbs./cu yd.) Cement	Fly Ash
L	610	---
LF1(15)	469	84
LF2(15)	496	86
LF3(15)	493	86
LC1(15)	444	78
LC2(15)	476	82
Average*	476 (δ = 22%)	83
LF1(25)	456	141
LF2(25)	440	137
LF3(25)	437	137
LC1(25)	430	135
LC2(25)	412	129
Average*	435 (δ = 28%)	136
S	610	---
SF1(15)	480	83
SF2(15)	500	87
SF3(15)	490	84
SC1(15)	456	79
SC2(15)	479	83
Average*	481 (δ = 21%)	83
SF1(25)	456	141
SF2(25)	430	134
SF3(25)	430	134
SC1(25)	444	139
SC2(25)	411	129
Average*	434 (δ = 29%)	135

Notes: * - calculated for fly ash concrete mixes only
δ - reduction in cement content as compared to the corresponding plain concrete

cement and fly ash, but it is clear that if the usual relationship of about 4 to 1 in prices of cement to fly ash prevails, the cost savings can be significant.

7.0 INFLUENCES OF FLY ASH ON FRESH CONCRETE PROPERTIES

Among the important influences that may be exerted by fly ash in concrete are effects on important properties of fresh concrete. The influence on rheology and water demand may be especially pronounced, but possible influence on air content, workability, and compactability, hence density of the final product, may also be noteworthy. The effects of fly ash on setting behavior of concrete have often been observed and may be critical in some circumstances, especially in winter concreting.

In this chapter we provide the results of measurements bearing on these aspects of fly ash effects.

7.1 Slump, VeBe Time, Air Content, and Unit Weight Measurements

A summary of the properties of the fresh concretes batched in this program is presented in Table 7.1-1. Each number in the table represents an average of at least six measurements performed on separate batches of the same composition. All of the mixes used in this study were designed to have a constant slump of approximately 3.0 in. and an air content of about 6%.

The data provided in Table 7.1-1 show that the actual results for slump and air content are very close to the target values. The recorded slump varied between 3.0 and 3.5 in., and the air content fell within the range of 5.9% to 6.8%. This confirms the efficiency of the proposed mix design method and its ability to control the proportioning process so as to assure the desired fresh concrete properties.

Table 7.1-1 Summary of results on fresh concrete.

Mix	Slump (in.)	VeBe (sec.)	Unit wt. (lb/cu ft)	Air (%)
L	3.5	3.7	141.4	5.9
LF1(15)	3.1	2.6	140.7	6.4
LF2(15)	3.0	2.8	139.8	6.8
LF3(15)	3.3	2.7	142.3	6.6
LC1(15)	3.1	2.2	142.4	6.4
LC2(15)	3.0	2.4	142.0	6.6
LF1(25)	3.4	3.3	139.0	6.0
LF2(25)	3.5	2.8	140.2	6.3
LF3(25)	3.2	2.6	139.7	6.6
LC1(25)	3.5	2.4	141.0	6.5
LC2(25)	3.2	2.0	141.2	6.6
S	3.5	3.9	141.5	5.9
SF1(15)	3.1	2.8	139.8	6.8
SF2(15)	3.2	3.2	140.6	6.2
SF3(15)	3.0	2.8	140.8	6.3
SC1(15)	3.2	2.4	141.7	6.6
SC2(15)	3.0	2.6	141.9	6.1
SF1(25)	3.3	3.6	139.1	5.9
SF2(25)	3.0	2.7	140.2	6.5
SF3(25)	3.4	2.6	140.3	6.4
SC1(25)	3.5	2.8	140.5	6.5
SC2(25)	3.0	2.5	141.1	6.6

As described in Chapter 5, the mix design method aimed at taking advantage of the water reducing/workability improving properties of fly ashes by loading a "constant quality" paste with the maximum amount of aggregate acceptable for a given set of initial design parameters. In addition to being able to provide for the desired slump and air content, this approach also resulted in very consistent concrete unit weights. As can be seen from Table 7.1-1 the unit weights varied only from 139.0 to 142.4 lb/cu ft. This is a narrow range, with the percentage difference between the lowest and highest value only about 2.4%. This consistent unit weight was achieved despite the fact that the density of the different fly ashes used in the concretes varied from about 2.0 to about 2.75 g/cm^3, a difference of about 38%.

Although, when judged solely on a slump basis, all of the concretes produced in the course of this investigation seem to have the same workability, a noticeable difference was observed in their finishability and placeability properties. In general mixes containing fly ash were somewhat easier to work with and easier to place and finish than plain concrete mixes. In addition they were also more coherent and less susceptible to segregation and bleeding.

While there is no direct method of quantifying these differences, it appears that some indirect indication of their magnitude can be obtained by measuring the VeBe time.

The results of VeBe time measurements performed on the mixes used in this study are summarized in Table 7.1-1. It is observed that the mixes containing fly ash containing mixes have lower VeBe times than the corresponding control mixes. The reduction in VeBe time varies with the type of fly ash, the type of cement, and the replacement percentage used. The available data do not provide a clear indication as to which of the above parameters is of greatest significance.

The shortest VeBe time (2.0 sec.) was recorded for a mix containing 25% of high calcium fly ash C2; the longest (3.6 sec.) for concrete containing 25% of very fine low calcium fly ash F1. The slump results for these two mixes were 3.2 and 3.3 in. respectively, indicating the relative insensitivity of the slump test when compared to the VeBe test.

There seem to be a very good correlation of the VeBe data with the "aggregate demand" of various mixes as discussed in section 6.2. In fact, when determined from Figures 6.2-1 and 6.2-2, the weight of aggregate required for a 3 inch slump vary according to almost exactly the same pattern as do the VeBe time values. In other words, the mixes having the lowest values of VeBe time could accommodate the largest weight of aggregate and still preserve the 3 inch slump.

The above observations indicate that all of the fly ashes used in this investigations favorably influenced workability of the mixes. Concretes made with such fly ashes will be easier to place, consolidate, and finish, and after hydration should give a more uniformly durable product.

7.2 Relations Between Foam Index Tests and Air Contents

One of the fresh concrete properties that may be affected by fly is the dosage level of air-entraining agent (AEA) needed to assure the specified air content. The "foam index" test, while not standardized, is one way to determine this for a particular fly ash - cement combination.

Accordingly, the foam index test was performed on cement - fly ash compositions corresponding to all of the 22 varieties of concrete tested in the course of this research program. As discussed in Section 4.2 this test involved the mixing of 20 grams of the cement - fly ash combination with 50 grams of water, adding the AEA one drop at a time, and observing the stability of foam produced on the surface of the mixture after 15 seconds of shaking. The "drop" used in these measurements had a measured volume of 0.031 ml.

The 20 gram portions of the cementitious materials were prepared by blending 17 grams of cement with 3 grams of fly ash for the 15% replacement level, or 15 grams of cement with 5 grams of fly ash for the 20% replacement level.

The results of the foam index test are reported in Table 7.2-1. The numbers listed under the FI heading represent the foam index, i.e. the minimum number of drops of the AEA which, upon adding to the suspension of a particular cement - fly ash blend in water, were able to produce a stable foam.

In order to help determine the usefulness of the foam index test in checking the AEA requirements of concrete made with different fly ashes, Table 7.2-1. also contains the amount of AEA (in ml/lb of cementitious material) added to each of the test concretes at the time of mixing, and the measured air content of the fresh concrete.

Table 7.2-1 Foam Index, AEA requirements and air content of fresh concrete.

Mix	Foam Index Test		Concrete Related Parameters		
	FI*	% change relative to control	AEA (ml/lb of cement. mat.)	% change relative to control	air content (%)
L	5	--	0.44	---	5.9
LF1(15)	9	80	0.88	100	6.4
LF2(15)	6	20	0.53	20	6.8
LF3(15)	6	20	0.53	20	6.6
LC1(15)	7	40	0.72	64	6.4
LC2(15)	5	0	0.47	7	6.6
LF1(25)	12	140	1.07	143	6.0
LF2(25)	6	20	0.56	28	6.3
LF3(25)	6	20	0.56	26	6.6
LC1(25)	7	40	0.68	55	6.5
LC2(25)	4	-20	0.42	-5	6.6
S	5	--	0.44	---	5.9
SF1(15)	10	100	0.96	118	6.8
SF2(15)	6	20	0.54	24	6.2
SF3(15)	6	20	0.56	28	6.3
SC1(15)	7	40	0.73	66	6.6
SC2(15)	5	0	0.50	14	6.1
SF1(25)	12	140	1.06	141	5.9
SF2(25)	6	20	0.55	25	6.5
SF3(25)	6	20	0.55	25	6.4
SC1(25)	7	40	0.70	58	6.5
SC2(25)	4	-20	0.40	-9	6.6

* No. of 0.031 ml drops required for foam stability

The results presented in Table 7.2-1 show that FI values for all but one of the cement - fly ash compositions were higher than the FI values for the corresponding cement alone. The only mixes for which FI was equal to or lower than that of a cement alone were the blends of cement and the high calcium fly ash C2. The reduced AEA requirement for mixes with this fly ash may possibly be related to the fact that this particular fly ash was found to have the lowest LOI of the fly ashes used in this project, only 0.3%.

The percentage changes in FI relative to the control value for the cement alone, varied from -20% for blends containing the C2 fly ash at 25% replacement level to +140% for blends with fly ash F1 at 25% replacement level.

The replacement level used may also influence FI. In Table 7.2-1 it is seen that for fly ash C2 the FI reduction is 0% at 15% replacement and -20% at 25% replacement; this is true for both cements used.

In order to determine the usefulness of the foam index test in predicting the AEA requirements of full scale concrete mixes, a comparison was made between the FI number and the percentage of air in the corresponding full-scale batches of fresh concrete produced with the given AEA dosage. The materials used in the production of concretes were all from the same stocks as used in the foam index test.

Analysis of the data from Table 7.2-1 indicates that, in general, the amount of AEA required to produce an air content of about 6% air content in freshly mixed plastic concrete was increased by the presence of fly ash. The largest increases (around 140%) were observed for the two concretes containing the low calcium fly ash F1. In contrast, the amount of AEA required in mixes containing high calcium fly ash C2 was either reduced (by a few percent) or only slightly increased (maximum 14%) as compared to the plain concrete mixes. The other two low calcium fly ashes (F2 and F3) caused only moderate increases in the required AEA dosage (between 20% and 28%); the increases observed in concretes containing high calcium fly ash C1 were close to 60%. The percentage changes cited above did not seem to depend on the replacement level used.

Comparison of the FI numbers with the observed AEA requirements indicates that both parameters respond appreciably to the specific fly ash used. These observations suggest that a relatively strong correlation should exist between the FI number and the AEA requirement for concrete.

A plot of relative change (in %) for AEA requirement vs. FI is shown as Figure 7.2-1. The excellent correlation is obvious, and the calculated value of the correlation coefficient (for a linear relationship) was 0.98.

7.3 Effects of Fly Ash on Concrete Setting Behavior

Initial and final setting time was measured for all 22 concrete mixes studied in this investigation. As is specified in ASTM C 403, the measurement is actually carried out on mortars sieved from the concrete rather than the concrete itself. The details of the method are described in Section 4.5.

The results are presented in Table 7.3-1. Each data point is an

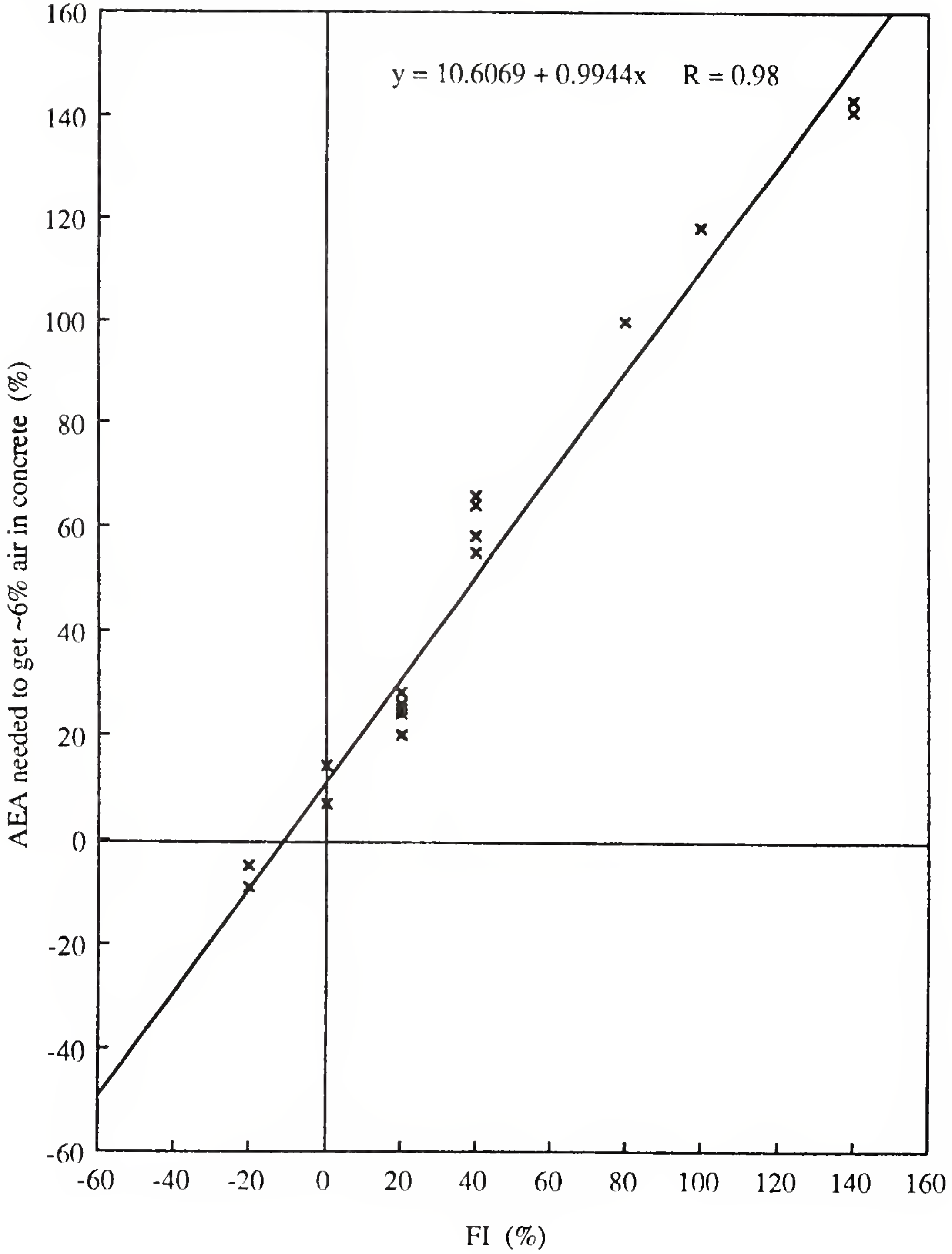

Figure 7.2-1 The relationship between the AEA needed to get ≈ 6% air in concrete and the Foam Index (FI).

Table 7.3-1 Setting time of concretes

Mix	Initial Set (hrs.)	Final Set (hrs.)	Retardation with respect to reference concrete			
			Initial Set		Final Set	
			(hrs.)	(%)	(hrs.)	(%)
L	3.4	5.0	---	--	---	--
LF1(15)	3.9	5.5	0.5	15	0.5	10
LF2(15)	4.4	5.3	1.0	29	0.3	6
LF3(15)	4.2	5.1	0.8	23	0.1	2
LC1(15)	6.9	8.2	3.5	103	3.2	64
LC2(15)	4.3	5.5	0.9	26	0.5	10
LF1(25)	4.2	5.5	0.8	23	0.5	10
LF2(25)	4.7	6.2	1.3	38	1.2	24
LF3(25)	5.3	5.8	1.9	56	0.8	16
LC1(25)	7.2	8.9	3.8	118	3.9	78
LC2(25)	4.7	6.0	1.3	38	1.0	20
S	4.6	6.3	---	--	---	--
SF1(15)	5.4	6.8	0.8	17	0.5	8
SF2(15)	5.2	6.8	0.6	13	0.5	8
SF3(15)	5.0	7.2	0.4	9	0.9	14
SC1(15)	7.5	9.5	2.9	63	3.2	51
SC2(15)	5.7	7.3	1.1	24	1.0	16
SF1(25)	5.0	7.0	0.4	9	0.7	11
SF2(25)	5.0	6.8	0.4	9	0.5	8
SF3(25)	5.1	6.8	0.5	11	0.5	8
SC1(25)	10.0	11.9	5.4	117	5.6	89
SC2(25)	5.5	7.0	0.9	20	0.7	11

average of three independent measurements. The data are also plotted in Figures 7.3-1 to 7.3-12. In these figures the graphs are assembled in groups of three, each group containing (1) the actual setting times (initial and final), (2) setting time increases above that of the reference plain portland cement concrete, and (3) the relative degree of retardation, expressed as a percentage.

As can be seen in the table, the initial set of the plain concrete batched with the L cement occurred 3.4 hours after mixing, and final set occurred at 5.0 hours. The corresponding values for plain concrete with the S cement were 4.6 and 6.3 hours respectively, indicating that cement S produces substantially slower setting than does cement L.

The addition of fly ash retarded the concrete setting time in all cases examined. For concretes made with type L cement, the measured time of initial set varied from 3.9 to 7.2 hours; the final set values ranged from 5.1 to 8.9 hours. For concretes made with type S cement, the range was from 5.0 to 10.0 hours for initial setting time, and from 6.8 to 11.9 hours for final setting time.

When compared on a relative basis (Figures 7.3-3, 7.3-6, 7.3-9 and 7.3-12) fly ash concretes made with cement L, which produces faster set in the absence of fly ash, in most cases show greater retardation than corresponding concretes made with cement S.

In general retardation produced by incorporating a given fly ash is proportional to the amount of fly ash used, being higher for higher percentages of replacement.

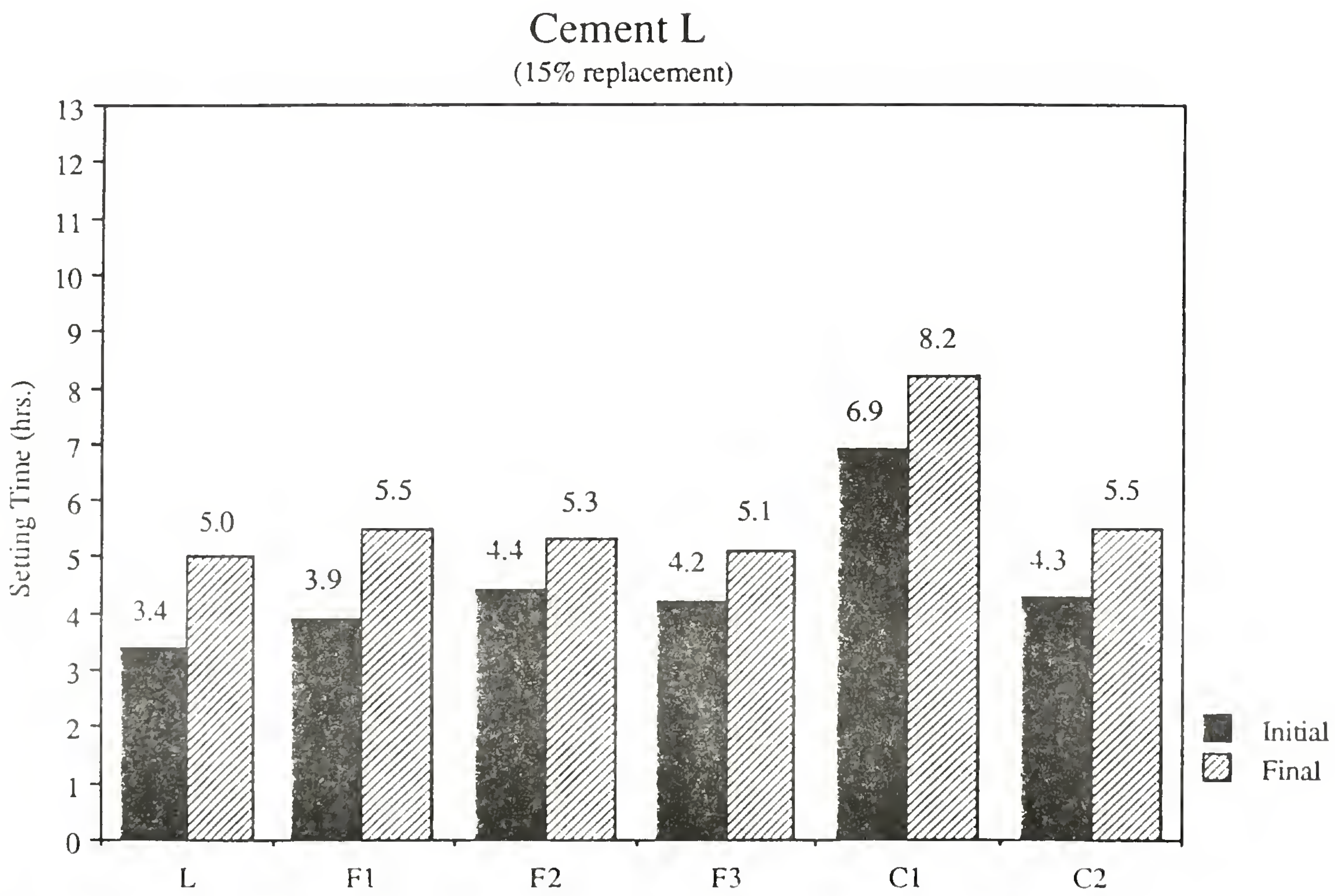

Figure 7.3-1 Setting time of plain and fly ash concretes, (cement L, 15% replacement).

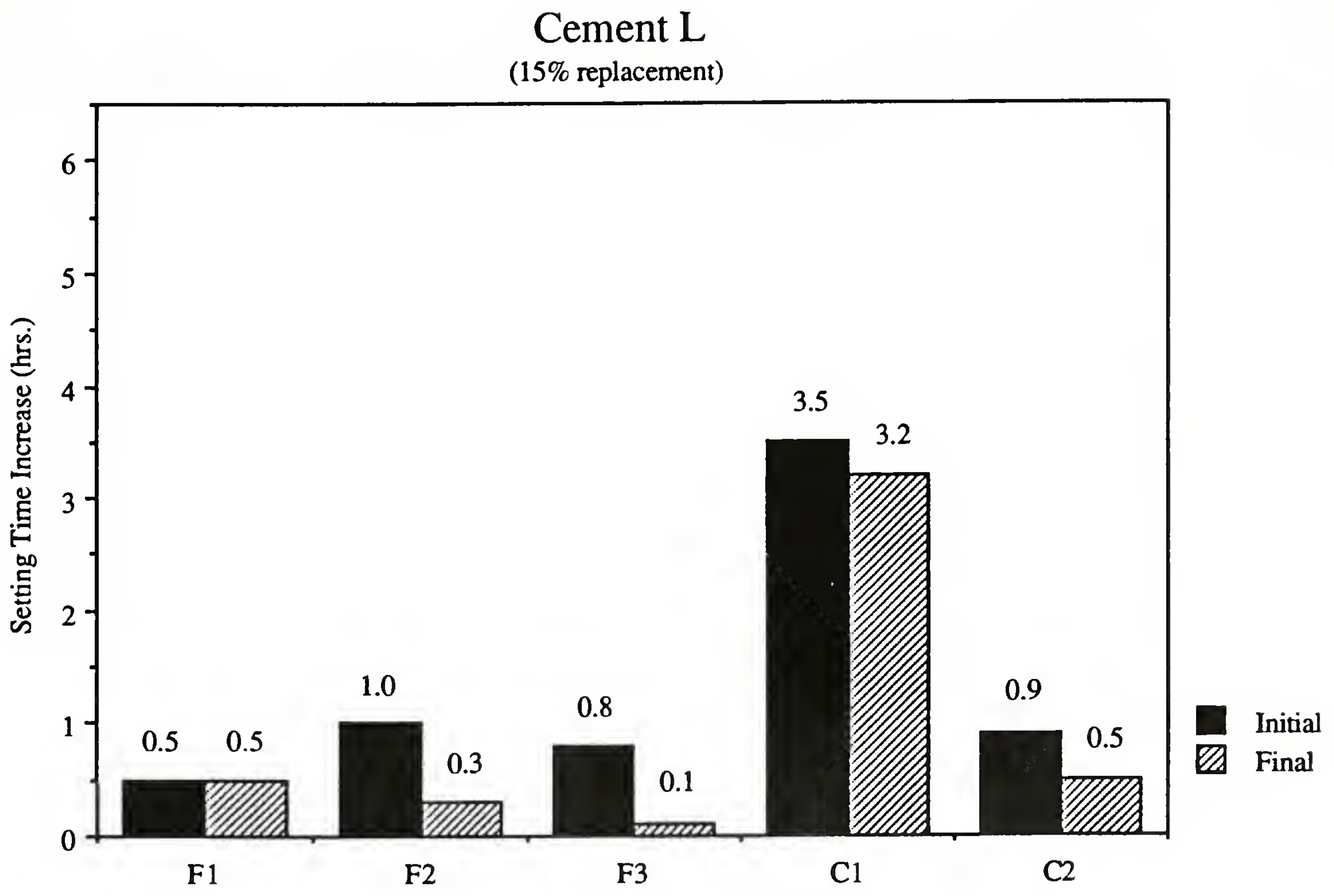

Figure 7.3-2 The increase of setting time of fly ash concretes as compared to plain concrete, (cement L, 15% replacement).

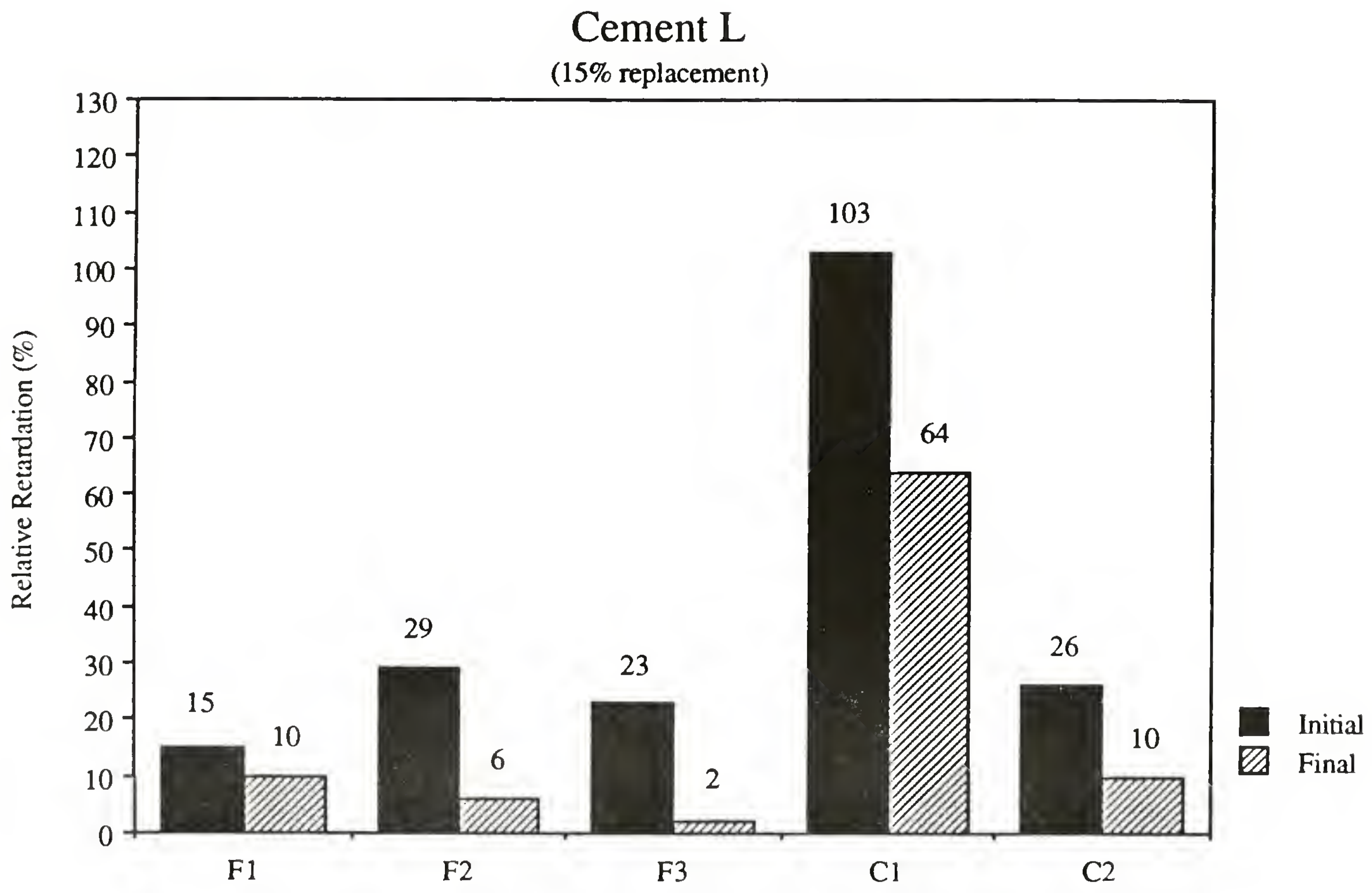

Figure 7.3-3 The relative retardation of fly ash concretes as compared to plain concrete, (cement L, 15% replacement).

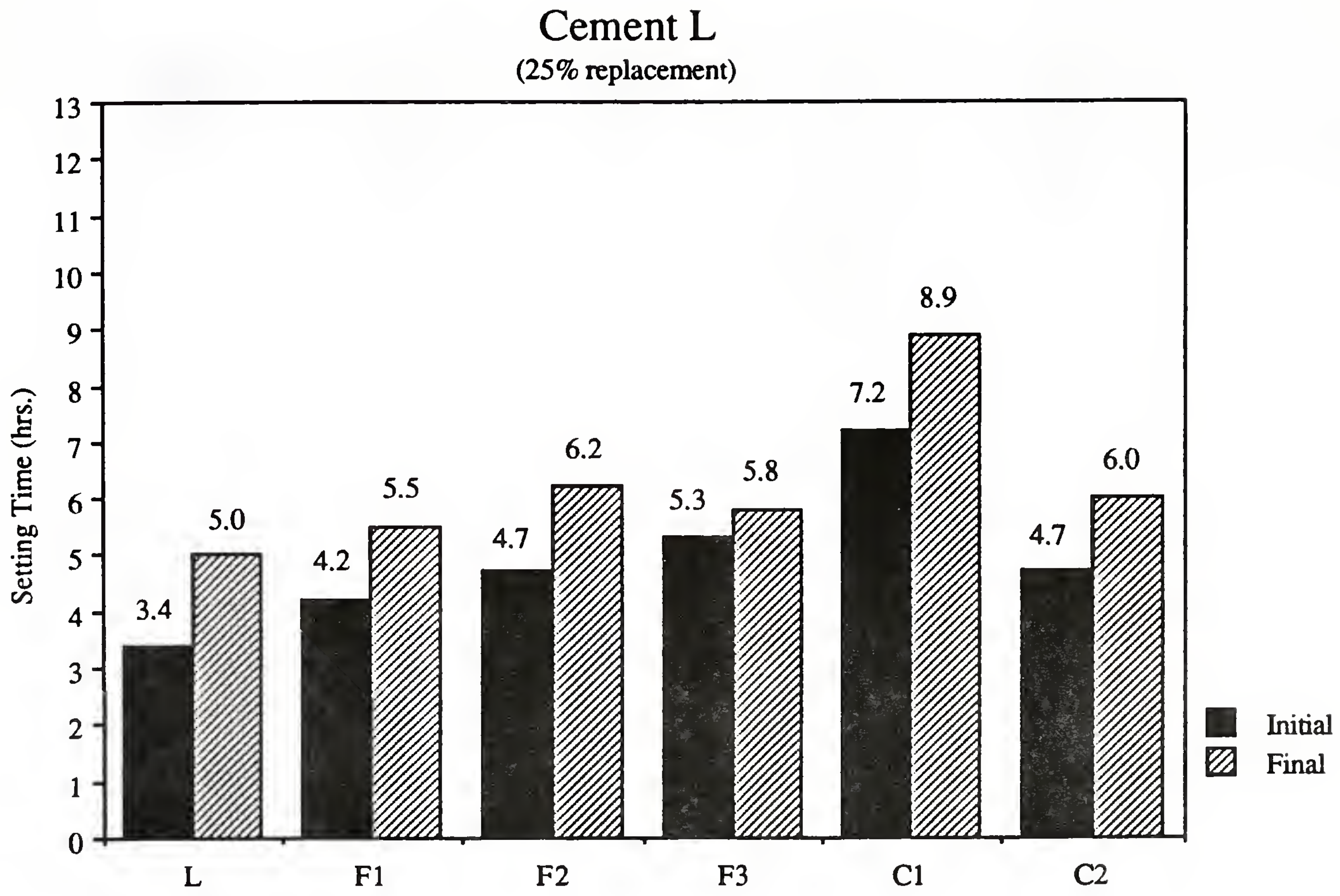

Figure 7.3-4 Setting time of plain and fly ash concretes, (cement L, 25% replacement).

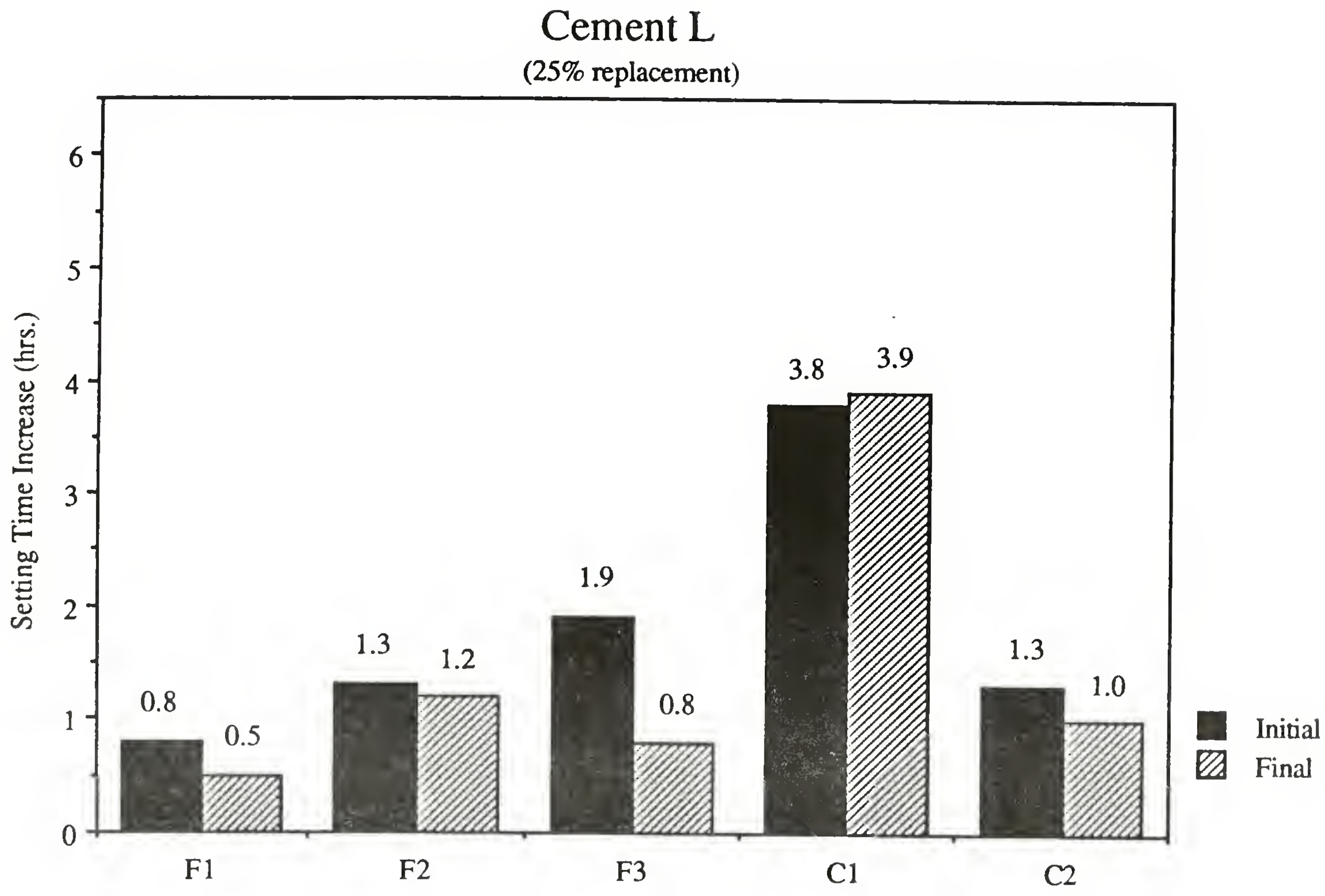

Figure 7.3-5 The increase of setting time of fly ash concretes as compared to plain concrete, (cement L, 25% replacement).

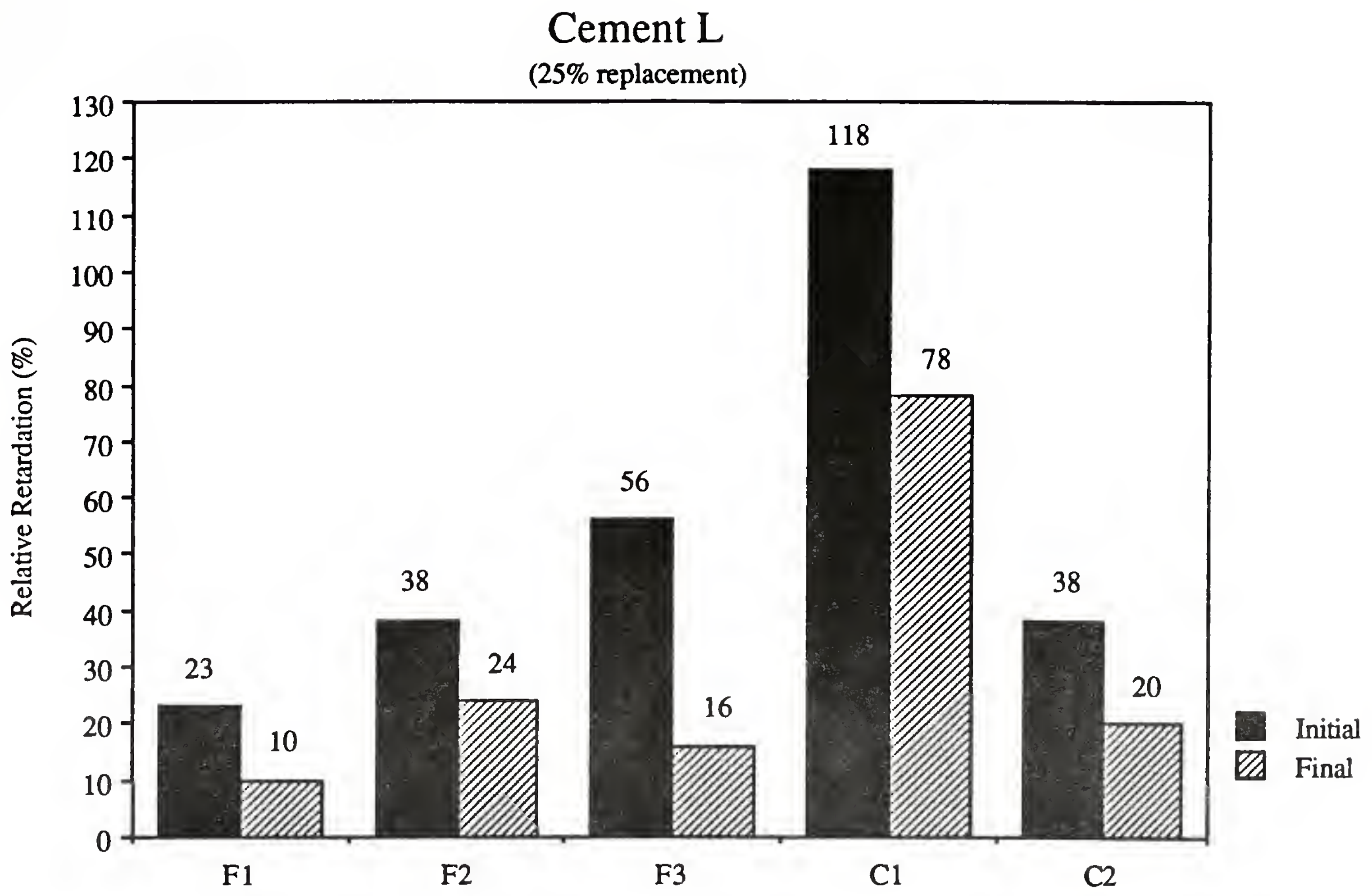

Figure 7.3-6 The relative retardation of fly ash concretes as compared to plain concrete, (cement L, 25% replacement).

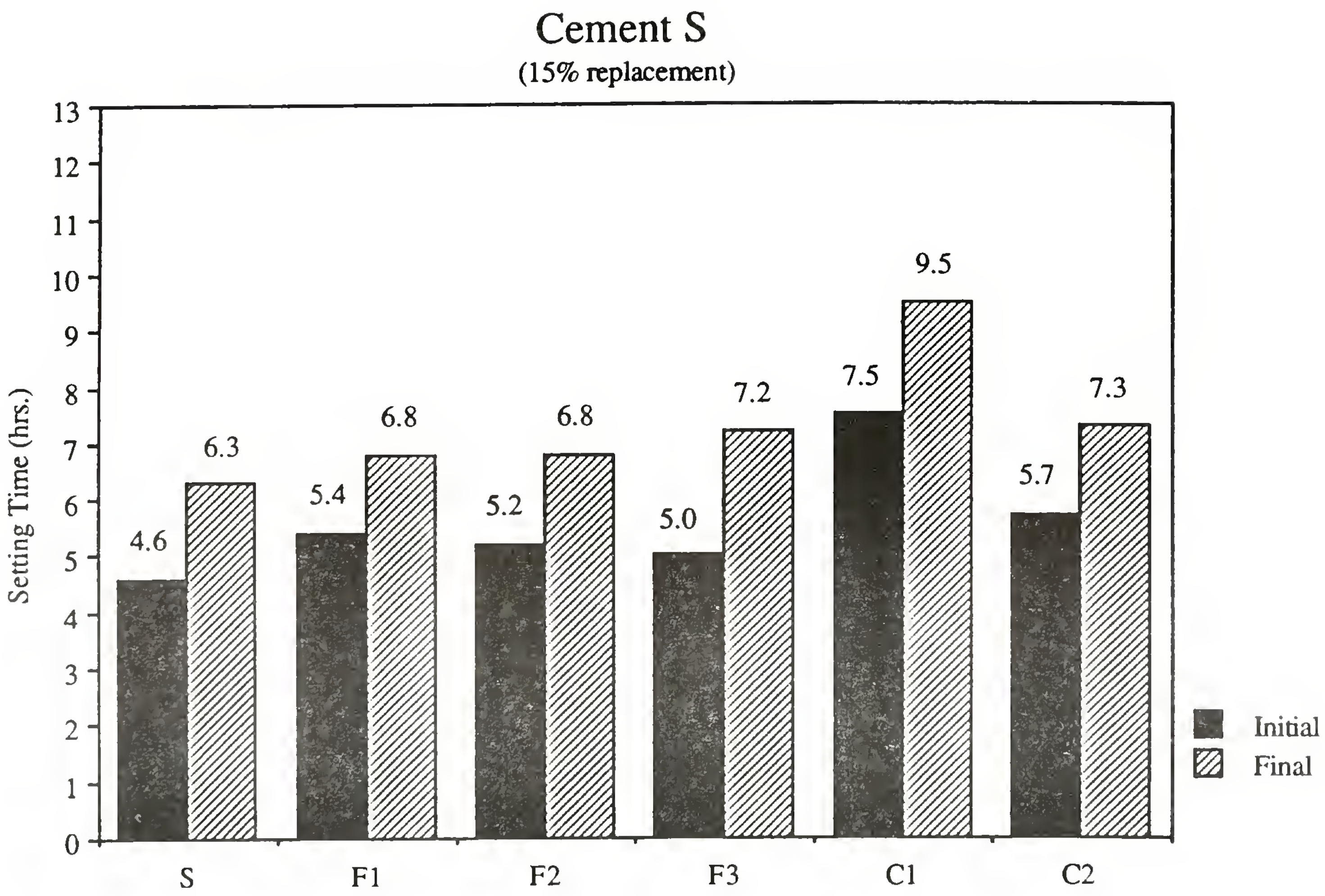

Figure 7.3-7 Setting time of plain and fly ash concretes, (cement S, 15% replacement).

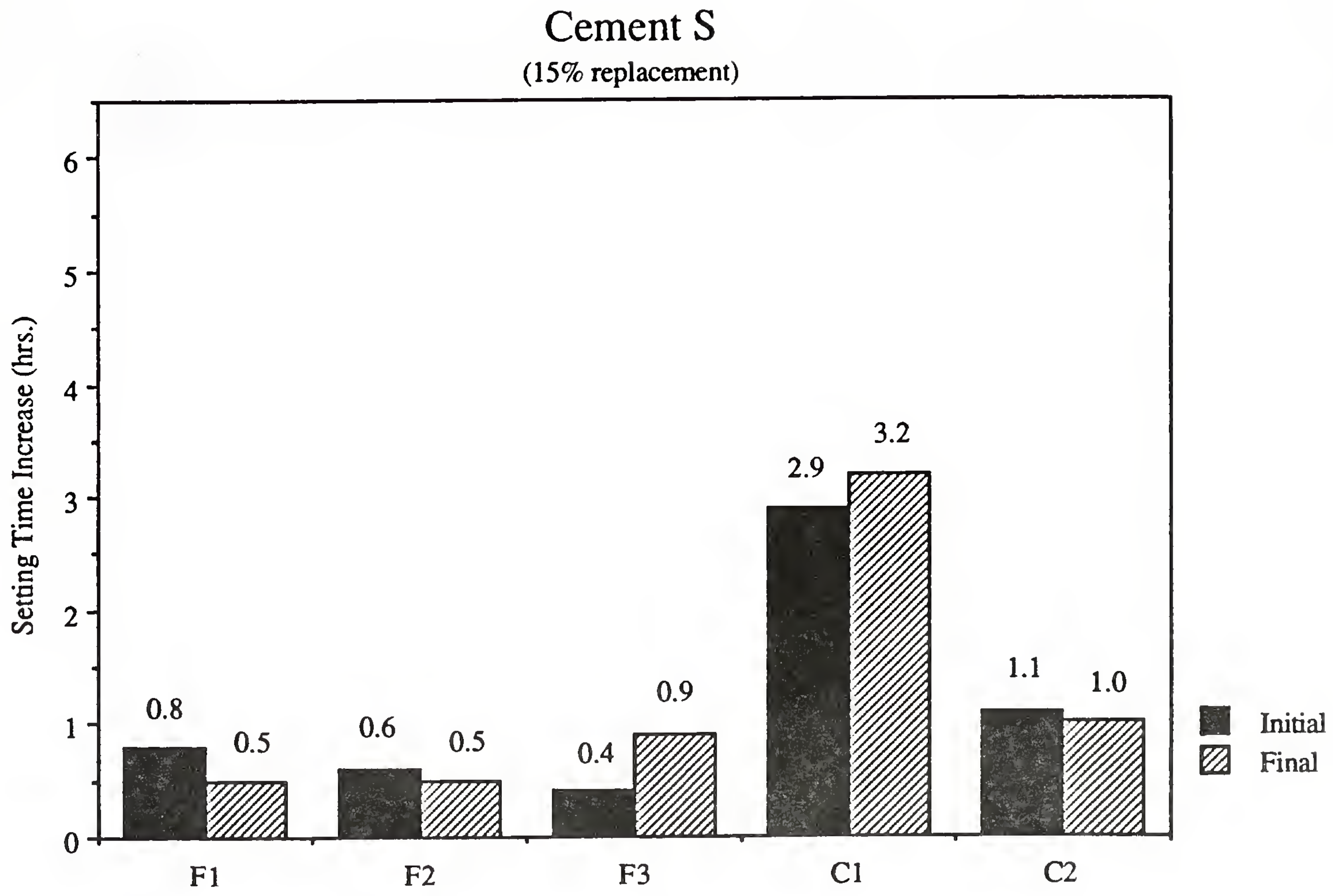

Figure 7.3-8 The increase of setting time of fly ash concretes as compared to plain concrete, (cement S, 15% replacement).

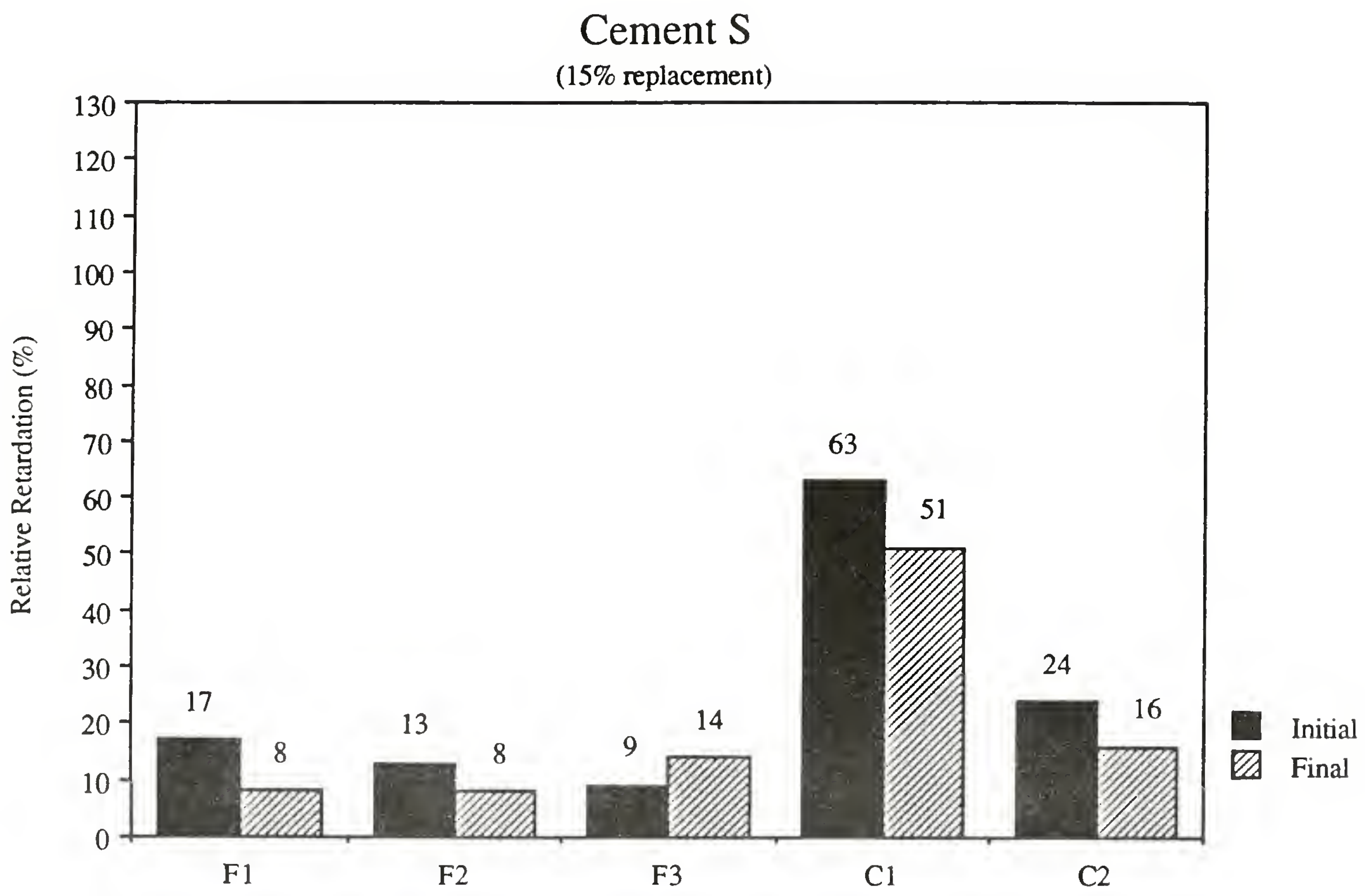

Figure 7.3-9 The relative retardation of fly ash concretes as compared to plain concrete, (cement S, 15% replacement).

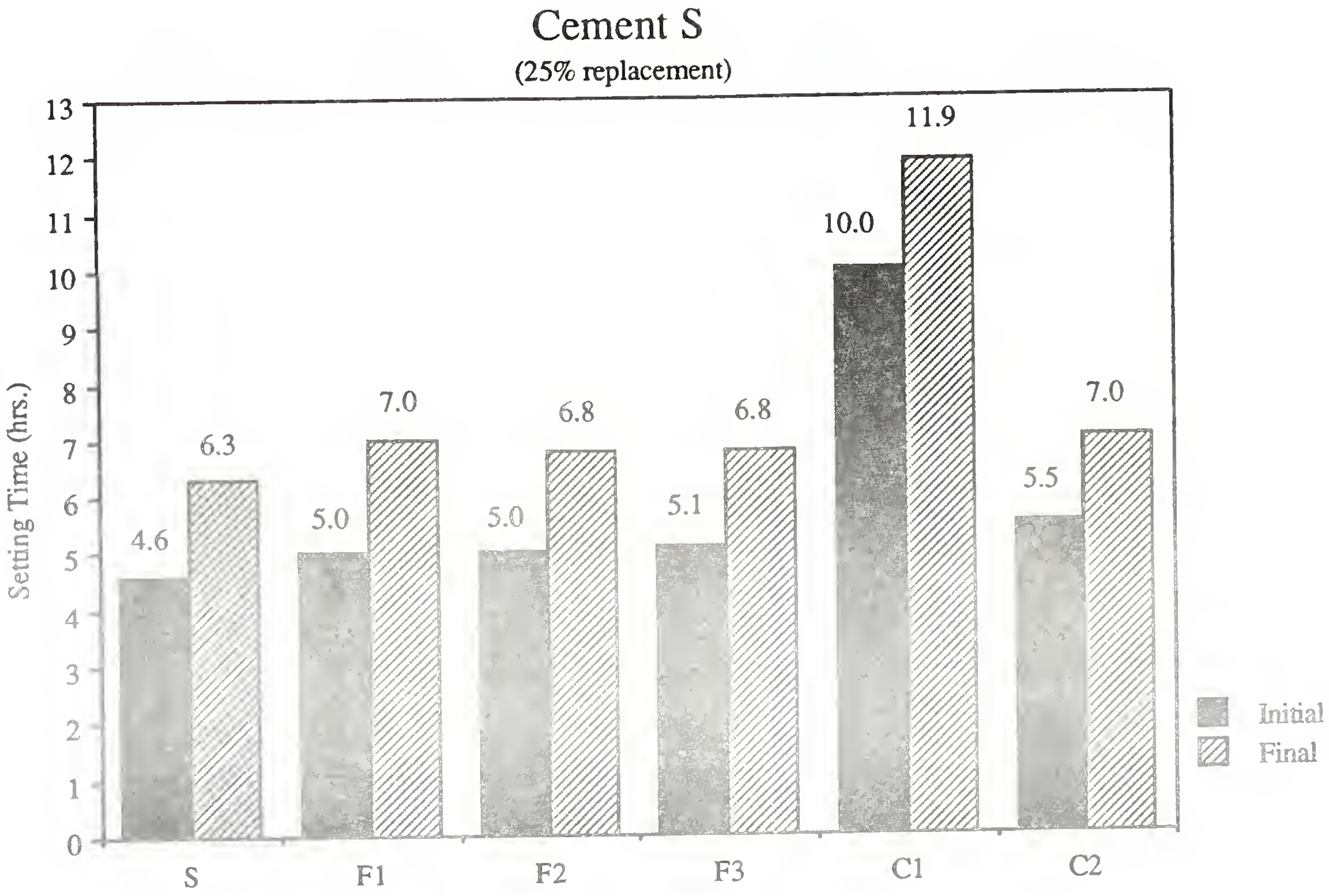

Figure 7.3-10 Setting time of plain and fly ash concretes, (cement S, 25% replacement).

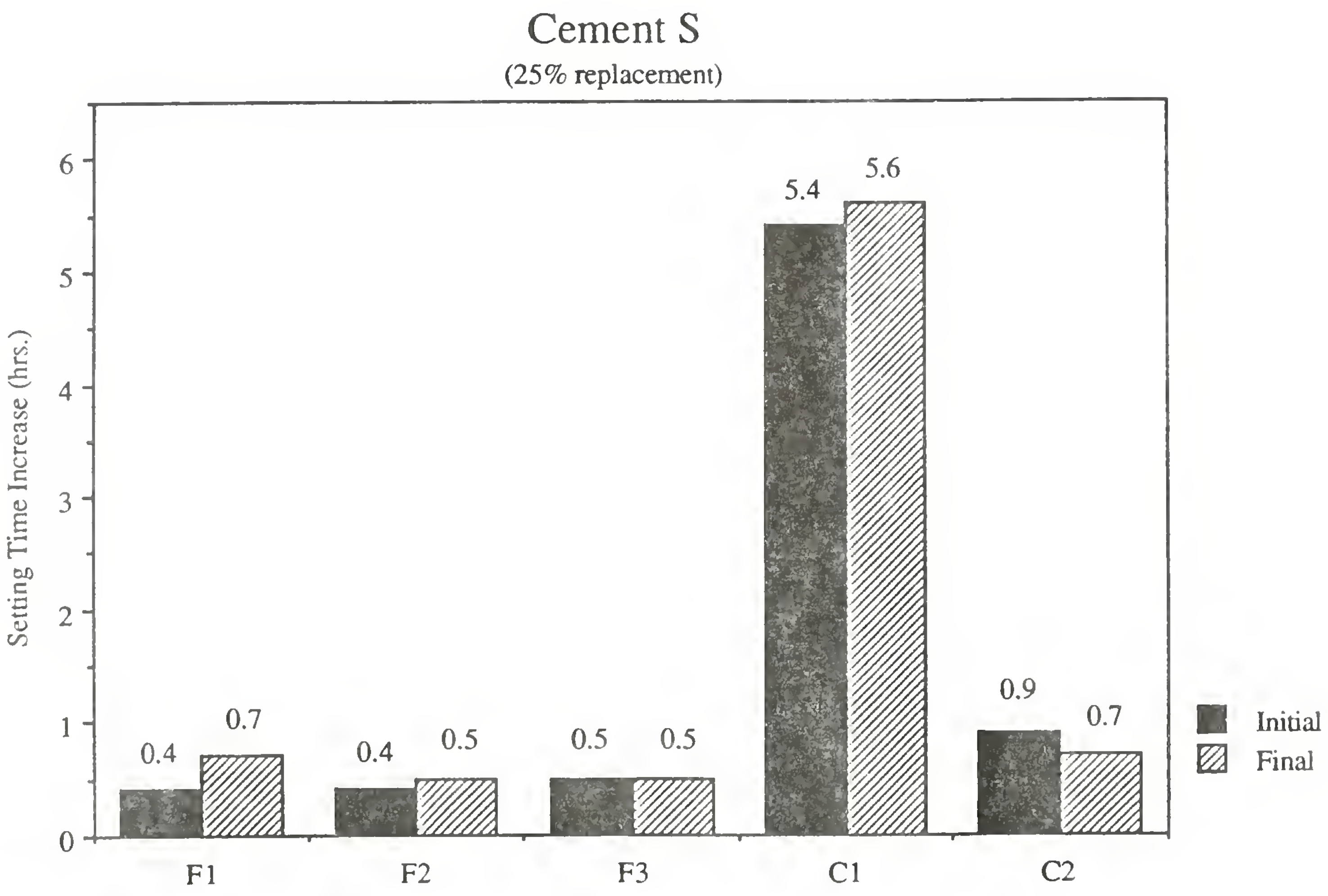

Figure 7.3-11 The increase of setting time of fly ash concretes as compared to plain concrete, (cement S, 25% replacement).

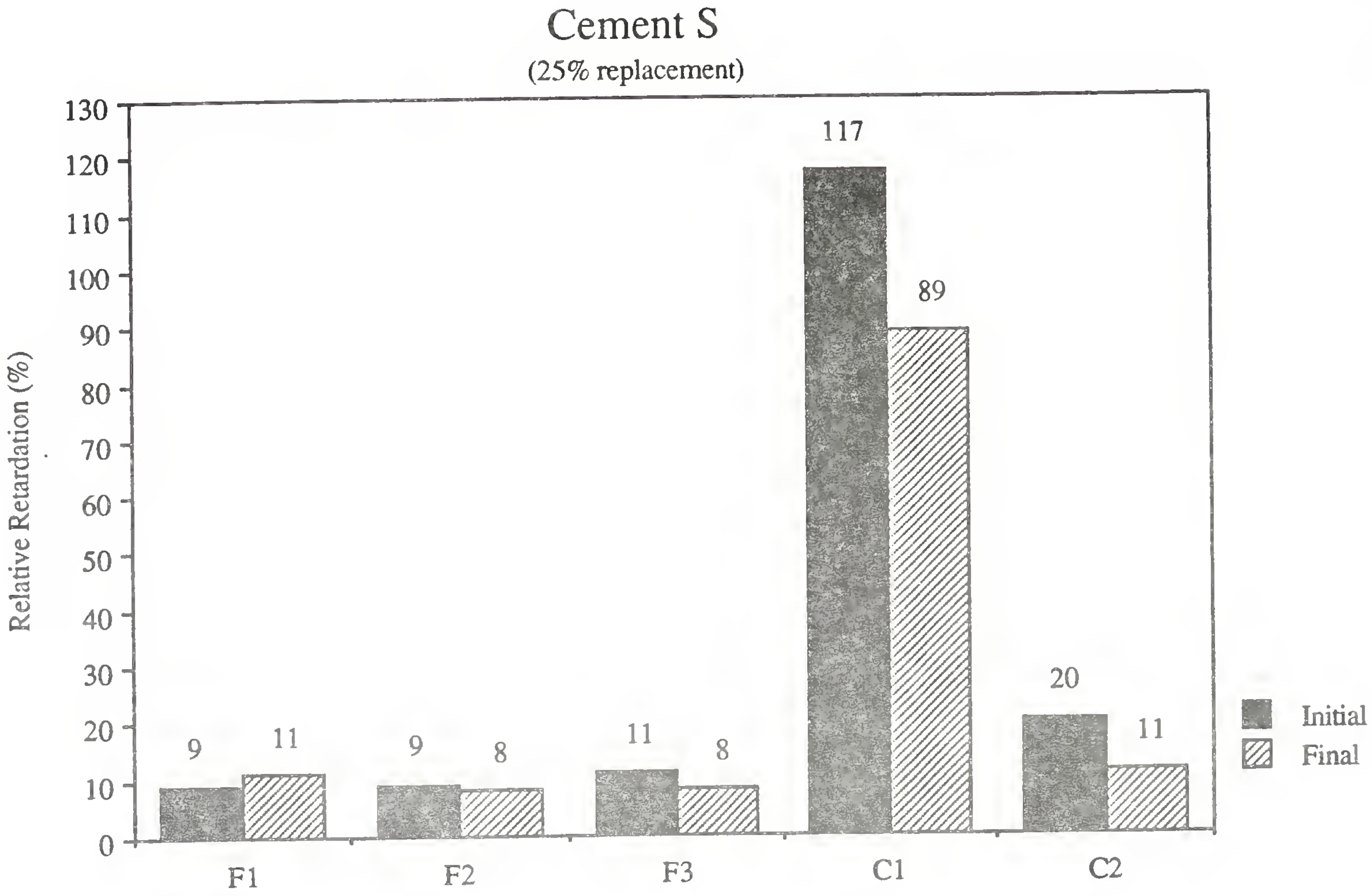

Figure 7.3-12 The relative retardation of fly ash concretes as compared to plain concrete, (cement S, 25% replacement).

There are also strong effects of individual fly ashes. Regardless of the type of cement and the replacement level used, the greatest retardation was always observed for concretes containing high calcium fly ash C1. The other fly ashes all show less pronounced effects, and among them the degree of retardation is virtually independent of the fly ash used.

8.0 INFLUENCE OF FLY ASH ON PROPERTIES MEASURED WITH FRESH CEMENT PASTE

In the previous chapter the effects of fly ash on certain important properties of fresh concrete have been reported. To some extent, the influence of fly ash on fresh concrete behavior derives from its effects on the fresh cement paste, which becomes a new combination of water with intermixed particles of portland cement and fly ash. As such, its characteristics are somewhat different from those of fresh plain portland cement without fly ash. To explore the differences in practice, measurements were carried out separately on the rheological effects and on the set retardation effects in cement pastes of the fly ashes used previously in concrete. Additionally, measurements were carried out of the influence of incorporating the fly ashes on the early hydration behavior of the system, as monitored by heat evolution - time calorimetric curves. These are studied much more effectively in pastes than in concretes, because of the thermal inertia provided in concrete by the large masses of the aggregate and sand components.

In these determinations the pastes themselves, while mixed separately, were designed to be closely identical to the pastes actually present in the concretes produced from the same components. They were batched from the same cements and fly ashes at the standard w:(c+fa) ratio of 0.49 used with the concretes. Mixing was carried out in a standard Hobart mixer, with the mixing sequence and scheduling specified in ASTM C 305.

8.1 Rheological Effects as Measured by the Minislump Cone

The rheology of fresh cement pastes is a fairly complex subject which has been the subject of much detailed scientific study, unfortunately without much practical insight being developed.

In the present research our efforts were confined to attempts at measuring the possible change brought about in cement paste rheology by the fly ash replacement for part of the cement. The measurements were carried out using the so-called "minislump cone", a downsized version of the standard slump cone that measures 2-1/4 in. in height and 1-1/2 in. in diameter at the bottom. The 60° cone angle of the standard slump cone is retained, but the dimensions are scaled down to be suitable for use with cement paste rather than with concrete.

The minislump cone test is not officially standardized, but it has been widely used in recent years. In the usual test, the measurement made is the increase in area covered by the slumped paste, rather than the residual height of the mass as is measured in the concrete slump test. This area is measured after lifting the cone and allowing the mass to spread. It is expressed as a percentage of the original area defined by the bottom of the slump cone itself. Thus the minimum measurement is 100%, if there is no spread at all. Most cement pastes spread out to some degree when the minislump cone is lifted, and the relative degree of spread serves as an indication of the relative degree of fluidity of the cement paste.

In these studies, measurements were made of the spread of pastes prepared with cement L and with each of the fly ashes combined with this cement at the 15% and 25% replacement levels, as previously defined. The w/c or w/(c+fa) ratio was 0.49 in each case. Each paste thus duplicated the composition of the corresponding paste in the concretes made with cement L.

The pastes were mixed in a standard Hobart mixer, using the mixing schedule specified for pastes in ASTM C 305. After initial mixing the pastes were allowed to rest undisturbed for 5 minute, then remixed briefly and placed in the minislump cone, the cone was removed, and the spread measured after 1 minute. Each measurement was made by caliper in two directions at 90° to each other, with the results averaged.

The results are shown in Figures 8.1-1 and 8.1-2 in the form of bar charts. Each result plotted is the average of three replicate determinations.

The measured spread area of the paste made with cement L itself averaged 269% of the area of the cone, an indication of the considerable fluidity of this w/c 0.49 cement paste. At the 15% replacement level, only the F2 fly ash produced any significant increase in spread area, to slightly over 300%. Of the others, the F1 ash actually produced a slightly reduced spread, while those for the F3 ash and both the C1 and C2 ashes were about the same as for cement L alone.

Not much difference was detected at the 25% replacement level. Again, the only substantial increase in indicated fluidity over the cement paste itself was that recorded for the F2 fly ash. The spread

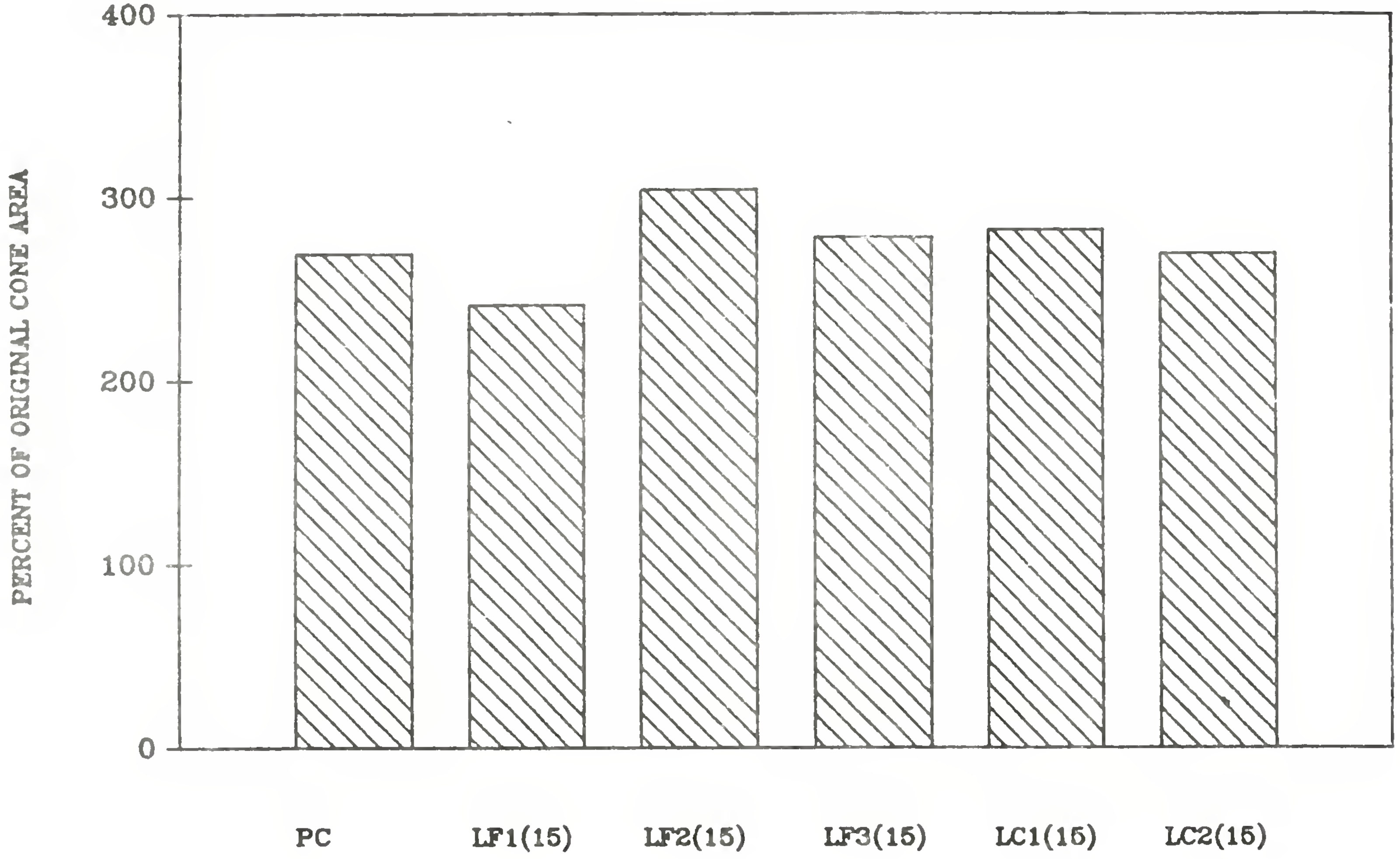

Figure 8.1-1 Minislump cone spreads, expressed in % of original cone area for portland cement L and fly ash pastes with 15% replacement.

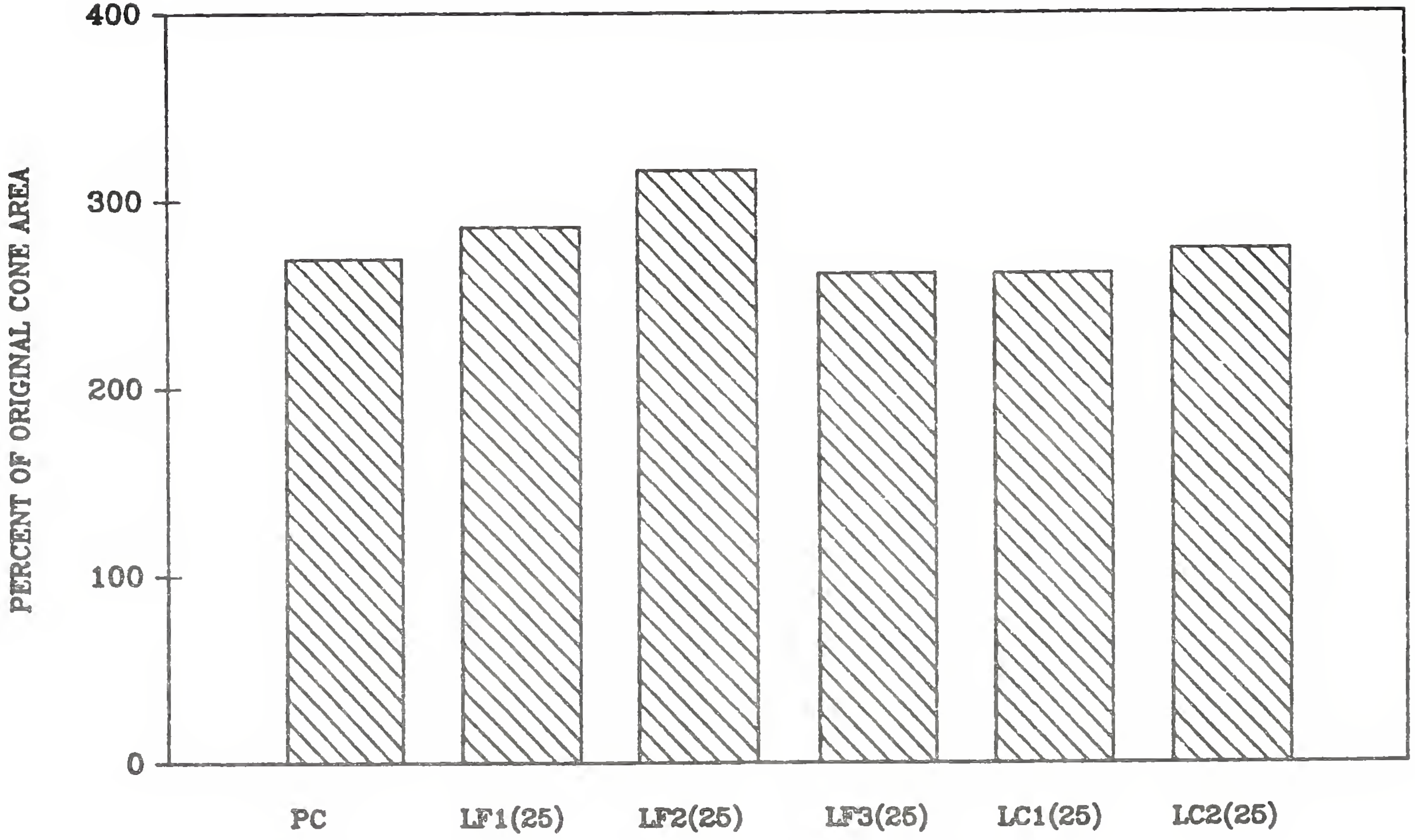

Figure 8.1-2 Minislump cone spreads, expressed in % of original cone area for portland cement L and fly ash pastes with 25% replacement.

area here averaged 316%, just slightly more than this fly ash produced at the 15% replacement level. Very slight increases over the spread area for cement L itself were recorded for the F1 and C2 ashes; with the other ashes no detectable effect was observed.

It appears that the minislump test does not provide a very sensitive indicator of the change in rheological behavior brought about by the inclusion of fly ash in the cement paste. Only fly ash F2 seemed to produce any real change in the fluidity as measured by the spread of the paste.

We believe that this essentially negative result is due to the nature of the test itself. In casual observations differences in effective fluidity between the fly ash pastes and the cement paste were noted if the paste pat was vibrated or subject to shock, such as is employed in Vebe testing of concrete or in flow table testing of mortars. However, such measurements are not standardized for pastes, and the matter was not pursued.

8.2 Effects of Fly Ash on the Setting Time of Pastes

Studies of the setting times of pastes were here restricted to pastes prepared with cement L, and batched at the single replacement level corresponding to 25% as defined for concretes. It was assumed that the influence of fly ash on the setting behavior of the system would be easier to detect at the higher replacement level.

The setting time determinations were carried out by the Vicat needle method as described in ASTM C 191.

The results of the setting time measurements are shown in

Table 8.2-1 and in Figures 8.2-1 to 8.2-3.

Table 8.2-1 Setting time of pastes.

Mix	Initial Set (hrs.)	Final Set (hrs.)	Retardation with respect to reference paste			
			Initial Set		Final Set	
			(hrs.)	(%)	(hrs.)	(%)
L	4.5	6.4	---	--	---	--
LF1(25)	6.8	9.0	2.2	49	2.6	40
LF2(25)	6.2	7.8	1.7	38	1.3	21
LF3(25)	6.0	8.0	1.5	32	1.6	24
LC1(25)	8.0	10.2	3.4	75	3.8	60
LC2(25)	6.7	8.2	2.2	48	1.8	28

As seen from these data, the setting time of all pastes containing fly ash is delayed when compared with setting time of plain cement paste. The extent of that delay depends on the specific fly ash used.

The time of initial setting of fly ash pastes varied from 6 to 8 hours; in contrast the reference cement paste showed initial setting in about 4.5 hours (see Figure 8.2-1). The time of final setting of the fly ash pastes varied from 7.8 to 10.2 hours, as compared to a final setting time of the reference paste of 6.4 hours. In other words, the replacement of 25% of cement with fly ash caused an increase in initial setting time ranging from 1.5 to 3.4 hours, and an increase in final setting time ranging from 1.3 to 3.8 hours.

Within the range of retardations exhibited, it was found that pastes with two of the three low calcium fly ashes (F2 and F3) had comparatively little retardation, their average increase being about 1.5

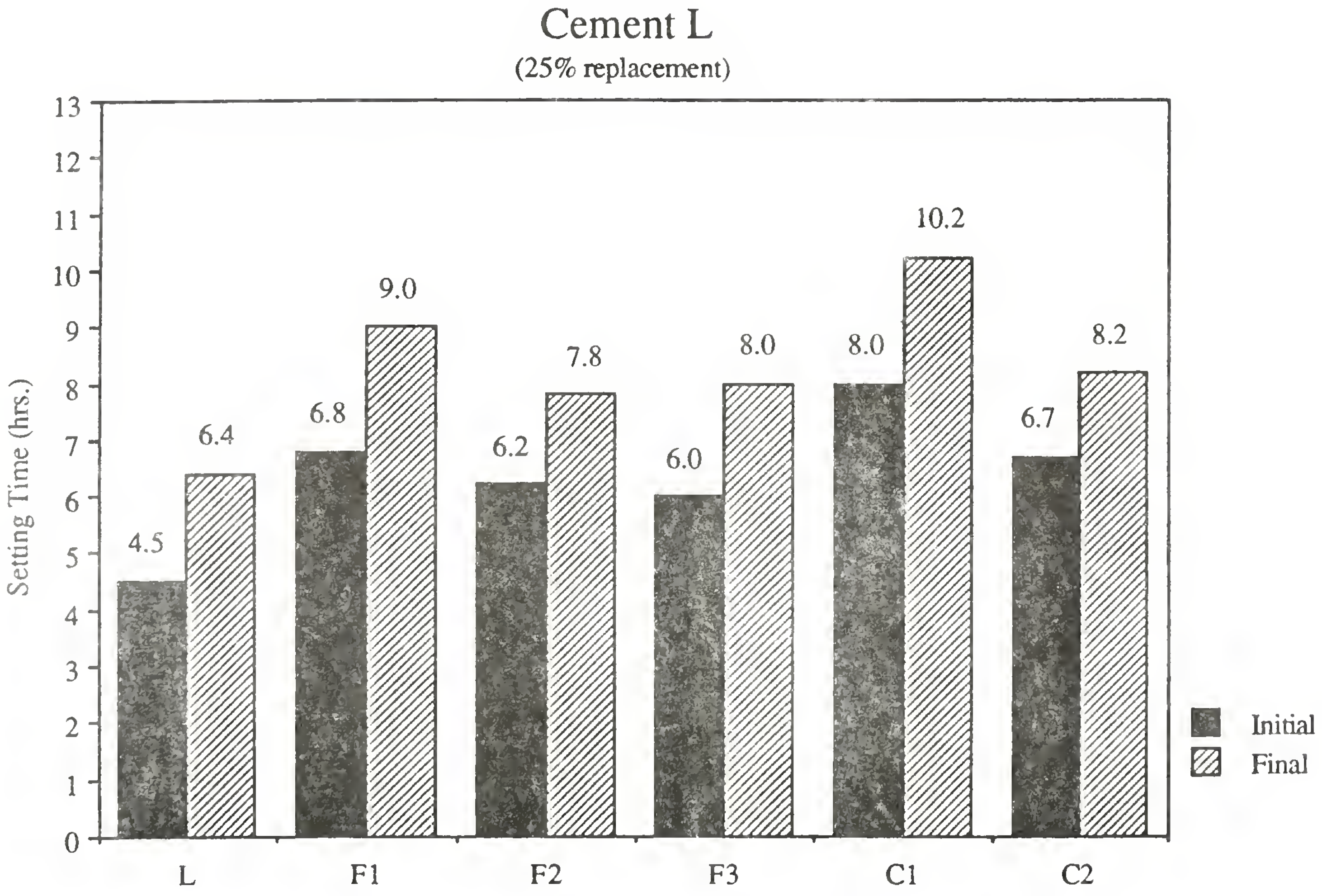

Figure 8.2-1 Setting time of plain and fly ash pastes used in this study.

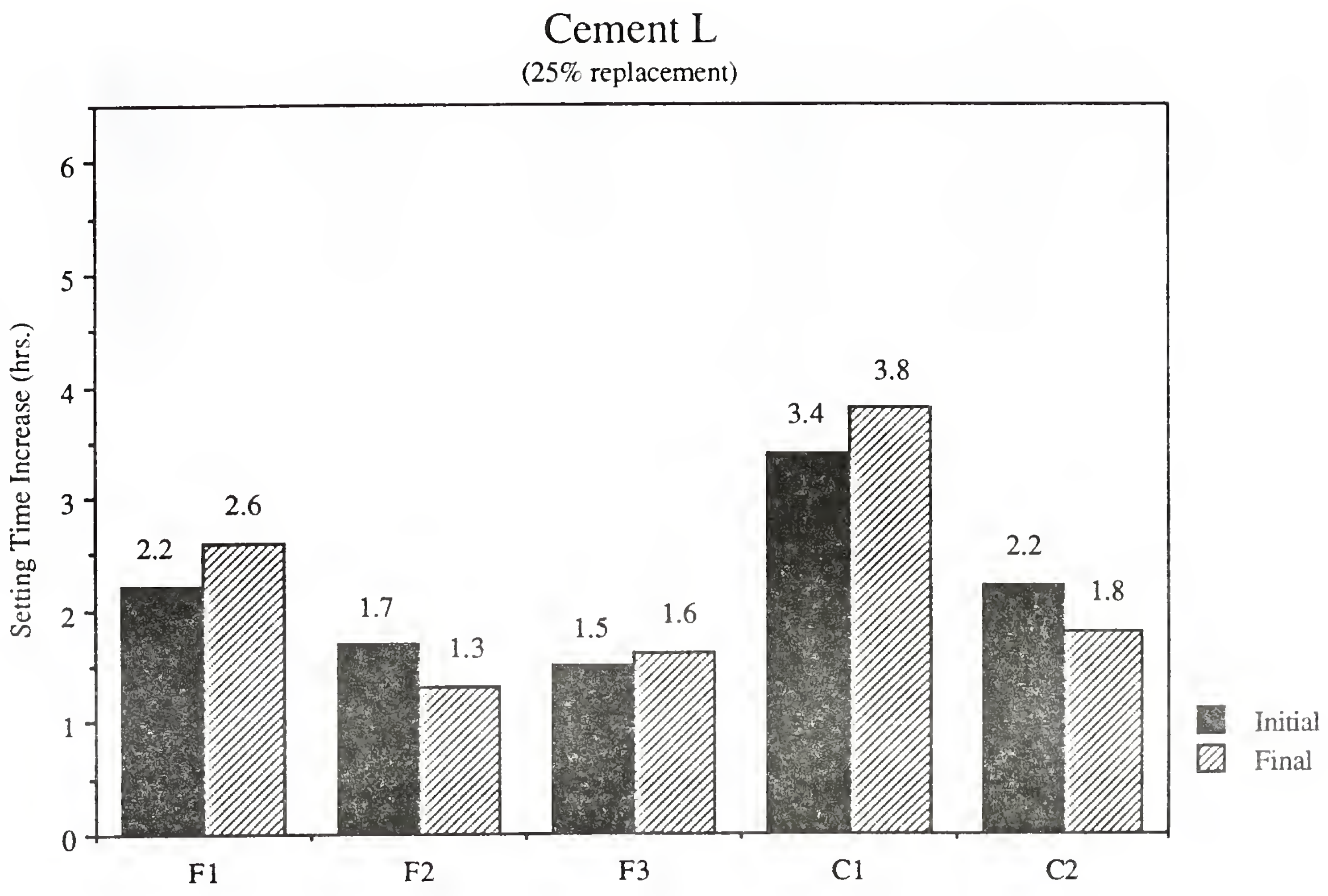

Figure 8.2-2 The increase in a setting time of fly ash pastes (as compared to plain cement paste)

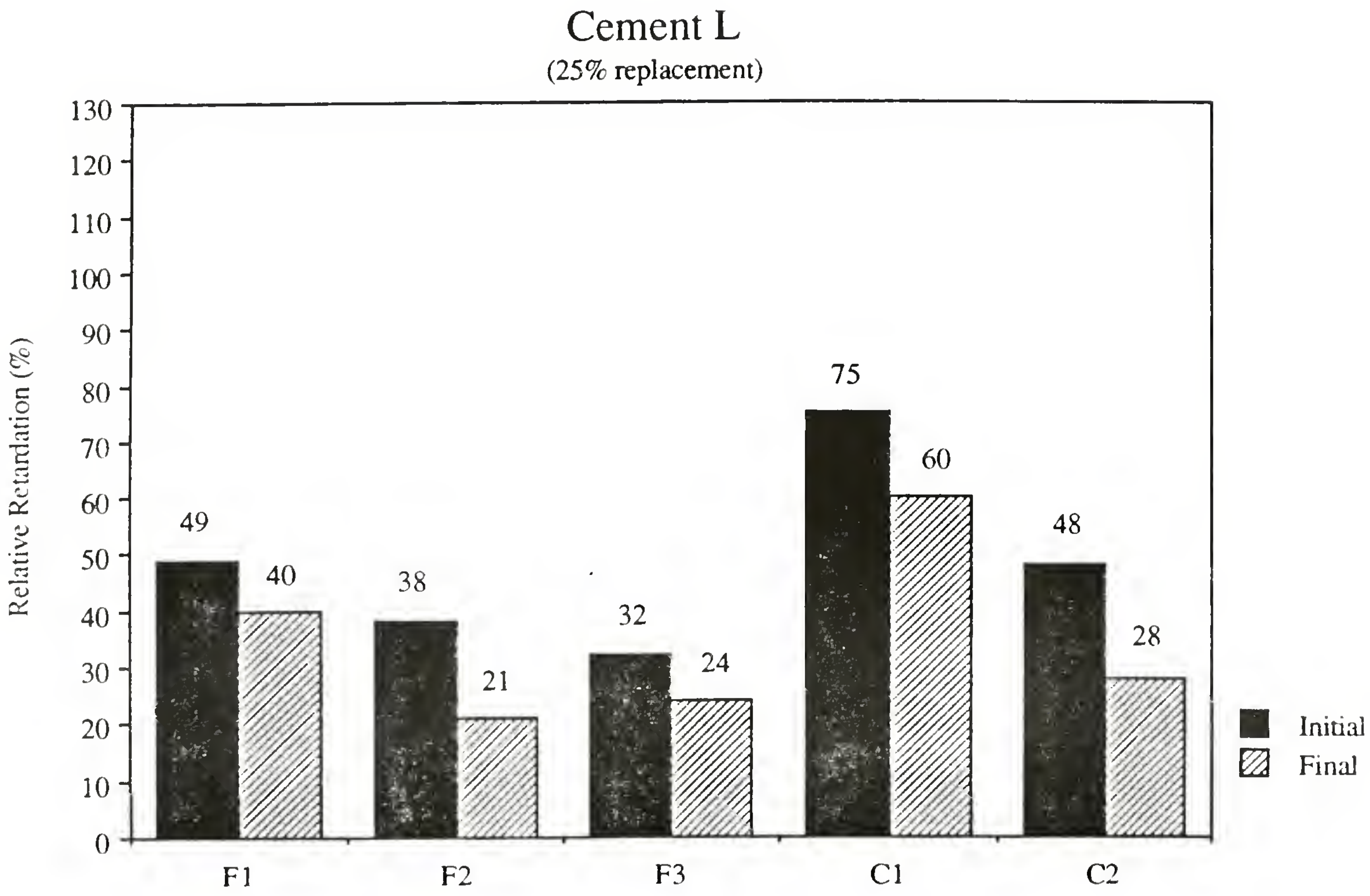

Figure 8.2-3 Relative retardation of fly ash pastes (as compared to plain cement paste).

hours. Paste containing low calcium fly ash F1 showed greater retardation, about 2.4 hours when calculated as an average for initial and final setting time values, and similar results were obtained with high calcium fly ash C2. Clearly the greatest degree of retardation, amounting to about 3½ hours, was observed for pastes made with the C1 high calcium fly ash.

The significance of these various degrees of paste retardation may be further illuminated by examining the data in terms of retardation relative to the setting times of the reference cement paste.
These relative retardations are presented in percentage terms in Figure 8.2-3.

It is apparent in this figure that again the effect of fly ash C1 stands out. Fly ash C1 produces a much higher degree of relative retardation than the others, of the order of 70% overall. The relative retarding effects of the other ashes are more modest, being about 40% or less. The figure also indicates that in all cases the percentage retardation of the final setting time was smaller than that of the initial setting time, the difference ranging from about 10% to about 20%.

8.3 Temperature Evolution of Pastes

The temperature evolution measurements described below were carried out with samples derived from the same batches of paste as were used for the determination of setting time.

The change in temperature occurring as a function of time for the first 14 hours or so of hydration was determined for these pastes under quasi-adiabatic conditions.

The apparatus used consisted of a styrofoam insulating box, two plastic containers (one for the paste under study and the other for a reference material), a set of two matched thermistors, a Wheatstone bridge and a strip-chart recorder. A schematic view of the apparatus and the test set-up is shown again for convenience in Figure 8.3-1.

In this method, in order to electronically cancel out fluctuations in the external temperature and humidity, the thermistor embedded in cement paste is matched against another thermistor embedded in an inert reference material, a mixture of 20-30 mesh Ottawa sand with water.

Immediately after each paste was mixed it was cast into the plastic specimen jar, and capped with a lids containing openings for the copper tubes carrying the thermistors. The thermistors were then inserted into the copper tubes which were in turn positioned through the openings in the lids. The bottoms of these tubes had been previously crimped shut, and approximately 1 ml of mercury was placed in each tube so as to surround the thermistor and improve heat transfer between thermistor and the wall of the copper tube. The thermistors were then embedded in the paste and reference material and connected to the Wheatstone bridge circuit.

As the hydration reactions increase the temperature of the paste system, the accompanying drop in resistivity of the thermistor is converted into a voltage difference between the two branches of the Wheatstone bridge circuit to which the paste and the reference thermistors were connected. This voltage difference is fed into a strip-chart recorder for a continuous readout. The system was previously

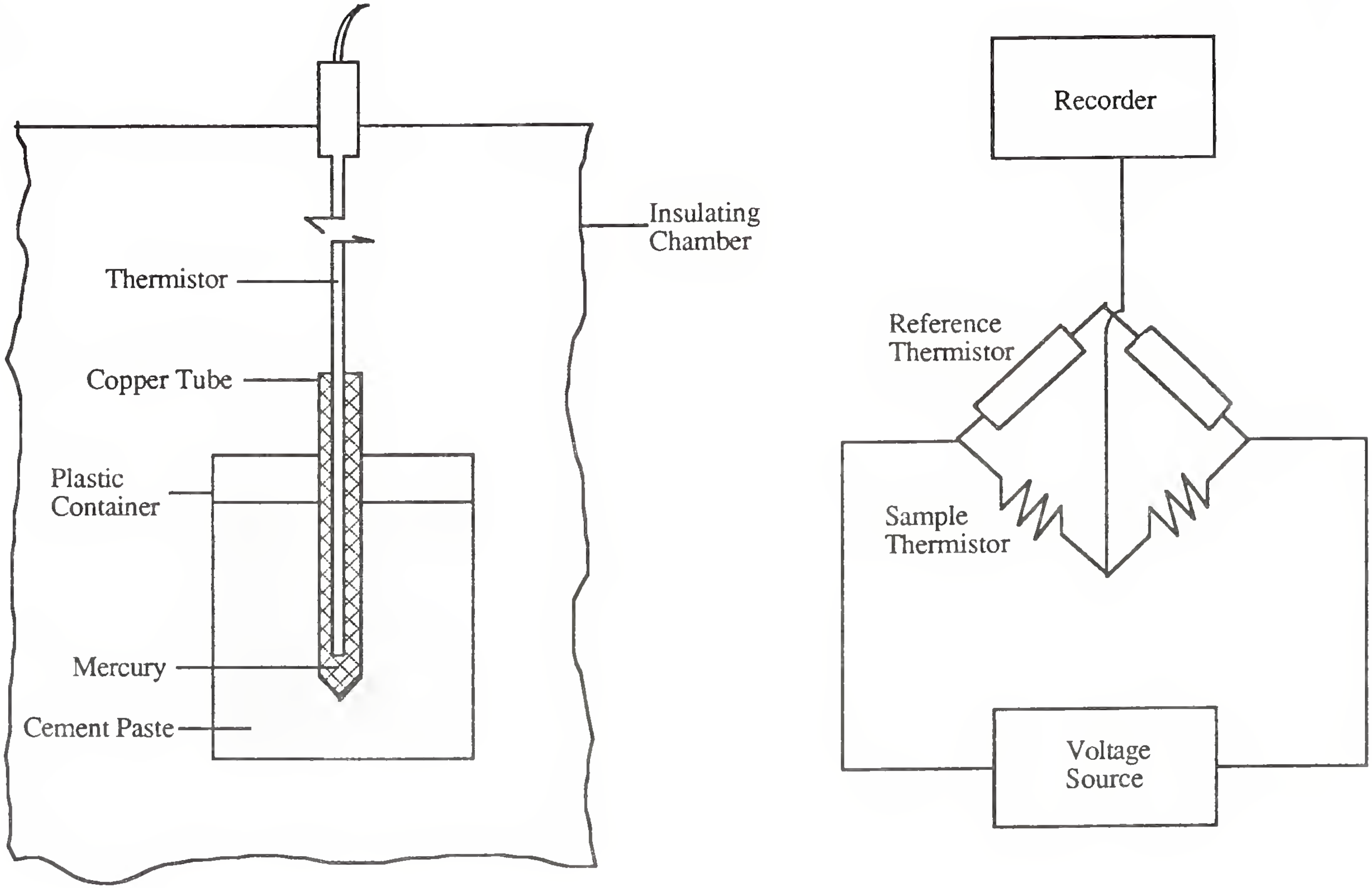

Figure 8.3-1 Schematic view of the apparatus used to measure the temperature evolution.

calibrated in order to establish the relationship between voltage difference and temperature change.

In all case the time needed for transfer of paste from the mixer into the temperature measuring device was kept as short as possible; the actual temperature measurements were able to be started about 5 minutes after the water was added to the dry cement-fly ash mix.

Two separate runs were performed for each type of paste. The averaged values of temperature attained at each time for the two runs are plotted vs. time in Figures 8.3-2 to 8.3-8. Again, only results for pastes made with cement L and with fly ash replacement at the 25% level are available.

Figure 8.3-2 shows all of the data in a single plot, for comparative purposes. Figures 8.3-3 through 8.3-8 show individual plots, with the times of initial and final set of the specific paste indicated on the plot.

All of the curves show a single temperature peak, with the time of the maximum being recorded anywhere from 8 to 12 hours after setting. The plain portland cement paste reached its maximum temperature at 8 hours; those of the fly ash-bearing pastes were delayed beyond this time to different extents.

The maximum temperature reached by the fly ash pastes was always less than that exhibited by the plain portland cement paste, the reductions ranging from 4° C to 9° C. The high calcium fly ashes produced much less reduction than the low calcium ashes.

The figures provided for the individual pastes show the relationships between times of initial and final set and the heat evolution

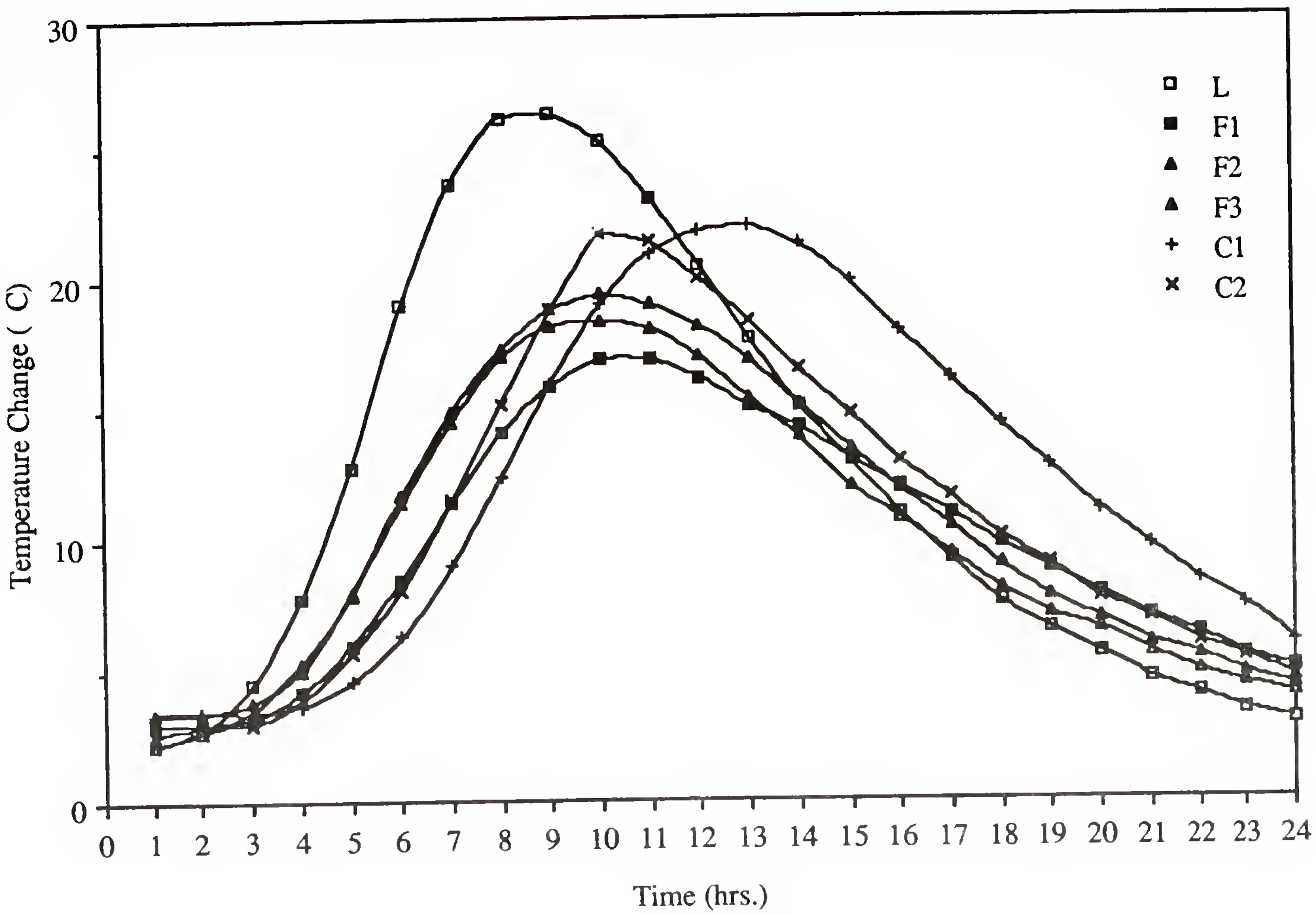

Figure 8.3-2 Heat evolution of plain portland cement and fly ash pastes as a function of time.

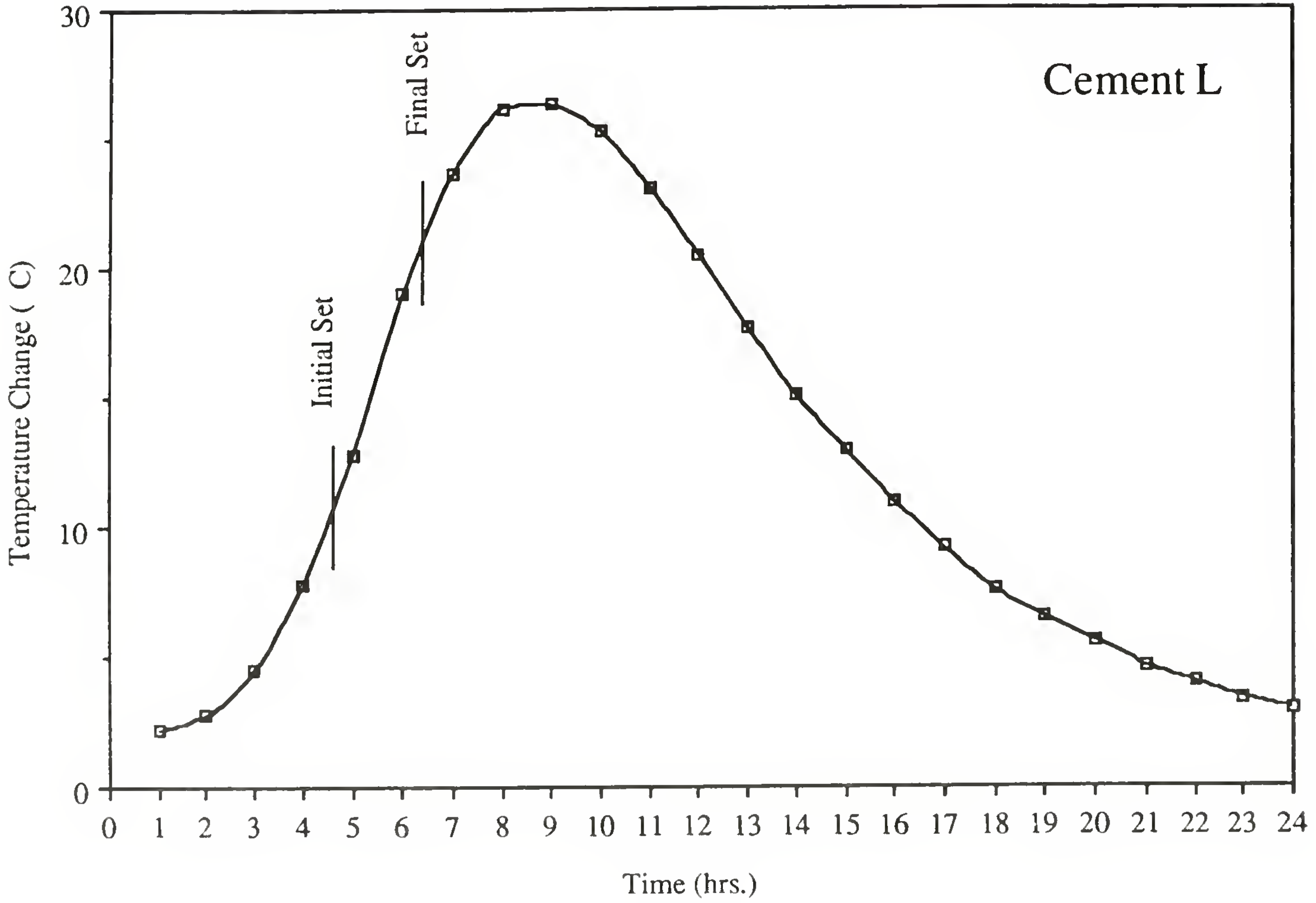

Figure 8.3-3 Heat evolution of plain portland cement paste as a function of time.

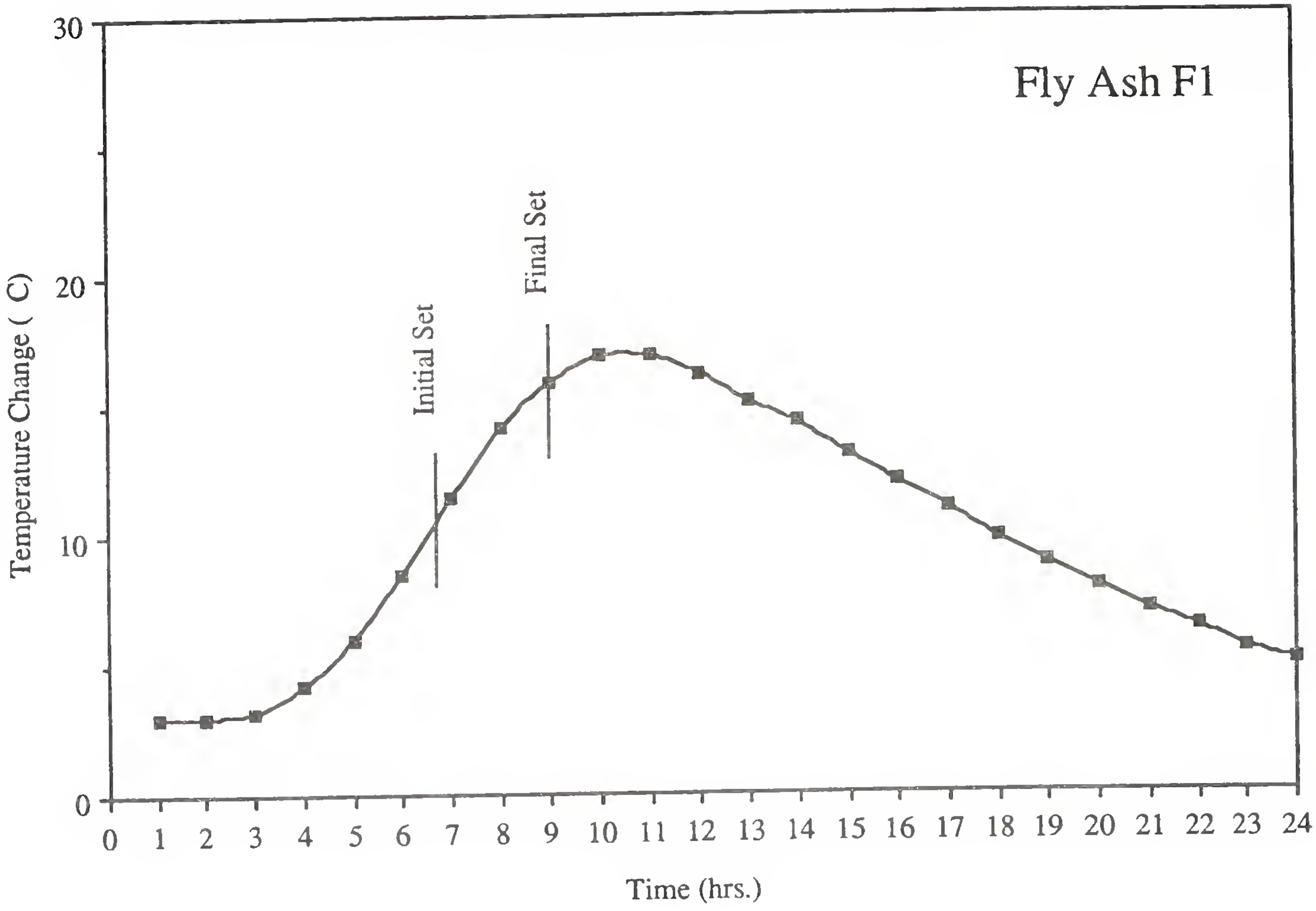

Figure 8.3-4 Heat evolution of fly ash paste as a function of time (fly ash F1).

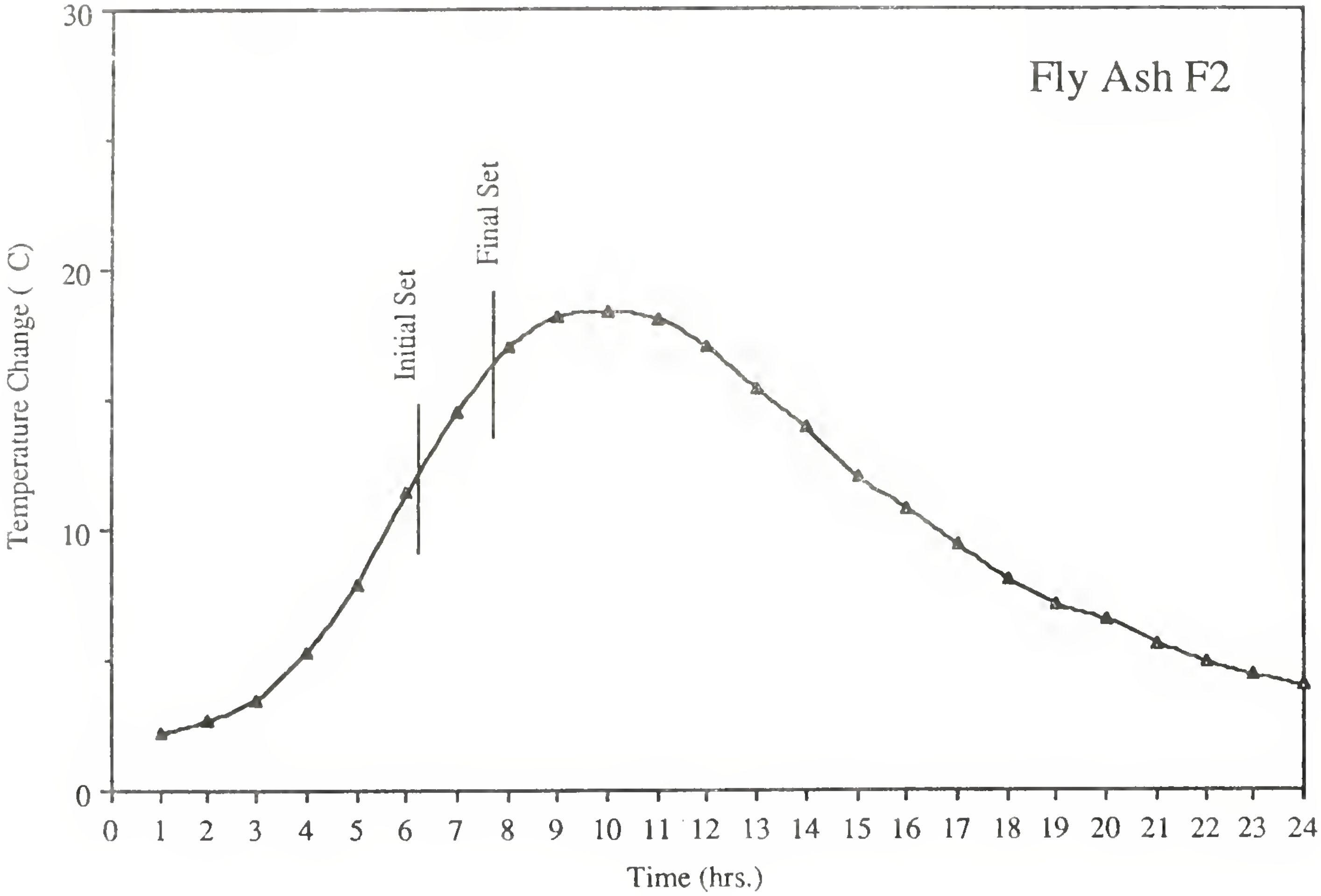

Figure 8.3-5 Heat evolution of fly ash paste as a function of time (fly ash F2).

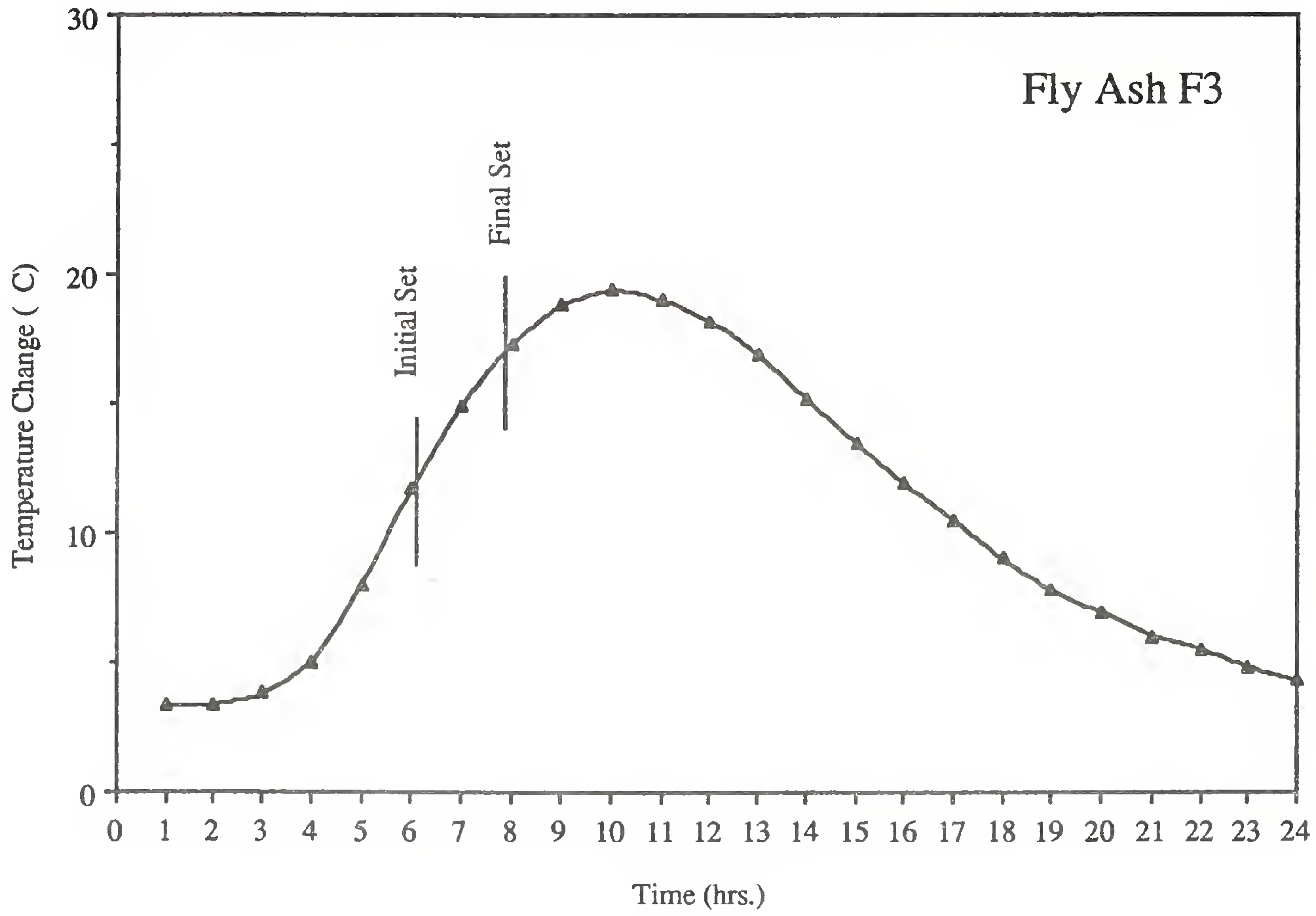

Figure 8.3-6 Heat evolution of fly ash paste as a function of time (fly ash F3).

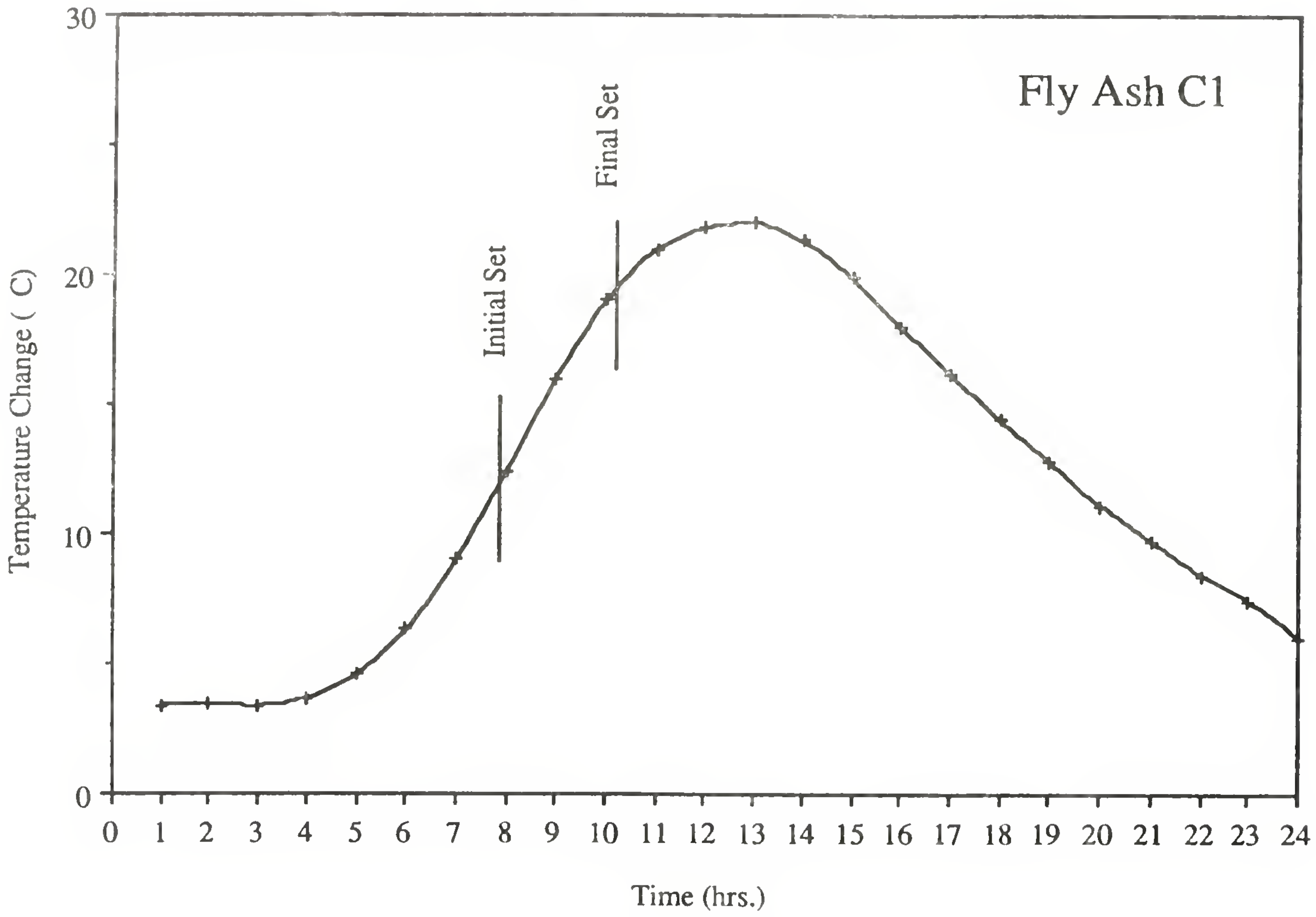

Figure 8.3-7 Heat evolution of fly ash paste as a function of time (fly ash C1).

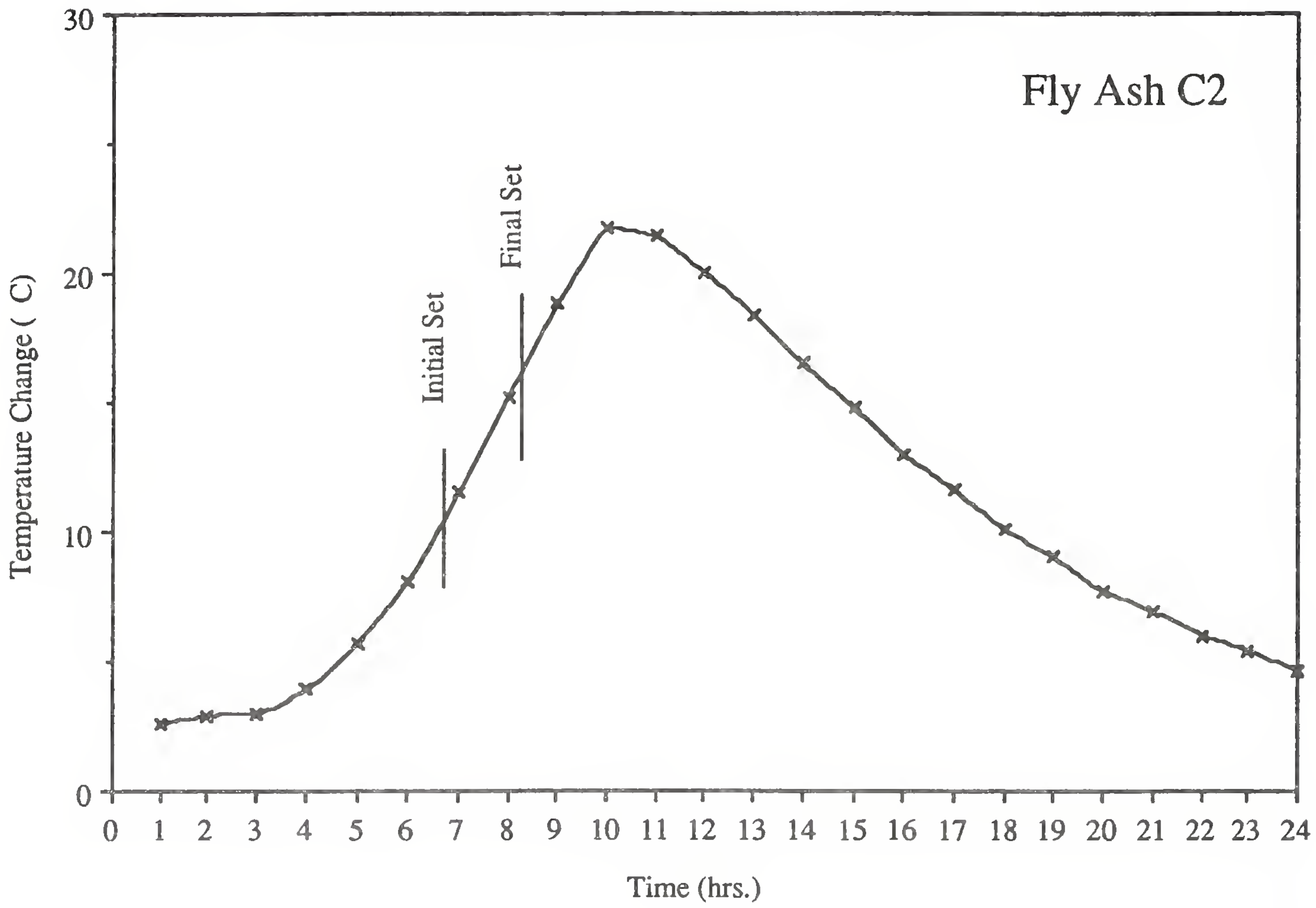

Figure 8.3-8 Heat evolution of fly ash paste as a function of time (fly ash C2).

curves. For the cement paste, initial set occurs at about one-third of the way up the heat evolution peak, and final set somewhat before the peak maximum. Similar trends are shown for the fly ash pastes except that initial set is rather higher up the curve, usually about half-way up rather than one-third of the way.

The figures also permit a quantitative evaluation of the dormant period, i.e. the period following the initial surge of heat evolution. This initial surge results in an immediate temperature increase of 3 or 4° C above the starting laboratory temperature. For a period of 1 to several hours, the hydration reactions are "damped" so that little heat is produced and no rise in temperature is experienced. At the conclusion of this dormant period, exothermic reactions resume at a considerable velocity, at the temperature starts to climb.

As indicated in Figure 8.3-3, the plain paste has a limited dormant period of the order of 1.3 hours. All of the fly ash pastes have longer dormant periods, with that made with the C1 high calcium ash being effectively dormant for 3.3 hours, i.e. about 2 hours longer.

Since the pastes used in heat evolution measurements were taken from the same mix batch as those used in the determination of setting time, an attempt was made to correlate the findings of these two tests, The results of such comparison are presented in Table 8.3-1.

Table 8.3-1 Comparison of temperature evolution and time of setting data for pastes used in this study.

Paste	Initial Setting		Final Setting		Heat Evolution Peak	
	Temp. (°C)	Time (hrs.)	Temp. (°C)	Time (hrs.)	Temp. (°C)	Time (hrs.)
L	10.5	4.5	21.5	6.4	26.4	8.5
LF1(25)	11.0	6.8	16.0	9.0	17.0	10.3
LF2(25)	12.0	6.2	16.4	7.8	18.4	9.9
LF3(25)	11.5	6.0	17.2	8.0	19.4	10.0
LC1(25)	12.5	8.0	19.7	10.2	22.0	12.7
LC2(25)	10.5	6.7	16.0	8.2	22.0	10.4

The reference cement paste shows initial set at 4.5 hours and a final set about 2 hours later. At this time of initial set the paste temperature in the quasi-adiabatic environment had risen 21.5° C above the starting laboratory ambient temperature (22° C), and was only 5° C lower than its maximum. The latter was not reached until about 2 hours after the time of final setting in the uncontrolled environment.

As discussed previously, the fly ash pastes seemed to follow the same general pattern, with some delay and with lower maximum temperatures.

It is worth pointing out that the fly ash pastes which reached temperature maximum most quickly (such as those made with F2 and F3 fly ashes) were also found to be least retarding, and the paste giving rise to the most delayed temperature maximum, C1, showed the greatest degree of set retardation.

The results discussed above seem to imply that the substitution of fly ash for part of cement changes the details of the heat evolution response, but the nature of the response is not altered. The mutual relations between setting time and temperature evolution found in fly ash pastes are similar to those observed in the plain paste, but are delayed and damped to various extents.

9.0 MECHANICAL PROPERTIES OF HARDENED CONCRETE

In this section we report the results of measurements of the various mechanical properties of hardened fly ash-bearing concrete, including static and dynamic elastic moduli, Poisson's ratio, compressive and flexural strength development, and density.

9.1 Static Modulus of Elasticity and Poisson's Ratio

As described in Section 4.9.4, measurements of static elastic modulus and Poisson's ratio were carried out on standard 6 in x 12 in. concrete cylinders. Two pairs of strain gages (longitudinal and transverse) were used to monitor strains developed by axial loading of the cylinders in compression. The recorded values of strains were averaged for each pair of gages and recorded.

The recorded data were analyzed with the aid of microcomputer using appropriate data processing and statistical programs (software courtesy of K. Kaufmann, School of Civil Engineering, Purdue University). The loads on the specimens were converted to stresses, and a least-squares regression analysis was performed in order to establish their relationship with corresponding strain values. In all cases a simple but accurate approximation (correlation constant $R \approx 0.999$) of this relationship was obtained using a linear regression model in which the best-fitting curve was assumed to be a straight line.

For the axial load - longitudinal strain relationship, the slope of this line gives the elastic modulus of the concrete in compression at the location of the strain gages. In the discussion that follows this modulus is referred to as the longitudinal modulus E_{long}.

The axial load - transverse strain relationship provides important information about the elastic behavior of the sample, and this value was used directly in calculation of the Poisson's ratio. In order to be consistent with the computer output, and to simplify the discussion which follows, the value of this "modulus" is here referred to as the "transverse modulus of elasticity", E_{tran}.

The values of the longitudinal elastic modulus and the transverse modulus of elasticity described above were then used in calculation of the Poisson's ratio by application of the formula:

$$\mu = \frac{-\varepsilon_{tran}}{\varepsilon_{long}} = \frac{\sigma}{E_{tran}} \text{ x } \frac{E_{long}}{\sigma} = \frac{E_{long}}{E_{tran}}$$

where:

μ = Poisson's ratio

ε_{tran} = transverse strains ($\mu\varepsilon$)

ε_{long} = longitudinal strains ($\mu\varepsilon$)

σ = stress (psi)

E_{tran} = "transverse" modulus of elasticity (psi)

E_{long} = longitudinal modulus of elasticity (psi)

All of the modulus of elasticity and Poisson's ratio values resulting from this experiment are summarized in Table 9.1-1. This table also gives auxiliary information, including the length of moist curing prior to testing, and the average compressive strength obtained for three cylinders cast from the same batch as the modulus specimens, and cured for the same period of time.

The data presented in Table 9.1-1 appear to be quite uniform and show only minimal scatter between the different specimens of the same mix. The recorded values of static modulus of elasticity (E_{long}) vary from 3.2 million psi to 5.6 million psi, depending on concrete strength. The corresponding values of Poisson's ratio vary from 0.170 to 0.236.

Both of these elastic constants determined on fly ash concrete specimens are well within the normal range (2 to 6 million psi for elastic modulus and 0.15 to 0.25 for Poisson's ratio) generally assumed for plain concretes.

Table 9.1-1 Experimental values of static modulus of elasticity and Poisson's ratio for concretes of different strengths.

Run	Mix	Age	Modulus of Elasticity (ksi) E_{long}	E_{tran}	Poisson's ratio $\mu = E_l/E_t$	Compressive strength (psi)
D01	SF1(15)	6 mths	5551	24529	0.226	6300
D02	SF1(15)	6 mths	5565	24119	0.231	6246
D03	LF2(15)	6 mths	5606	24398	0.230	6130
D04	LF2(15)	6 mths	5620	23815	0.236	6185
D05	SC2(15)	2 wks	4510	21474	0.210	4390
D06	SC2(15)	2 wks	4513	21361	0.210	4420
D07	SC2(15)	2 wks	4275	20834	0.205	4230
D08	SC2(15)	2 wks	4286	20821	0.206	4310
D011	SC2(15)	2 days	3239	19106	0.170	2640
D012	SC2(15)	2 days	3213	18275	0.176	2375

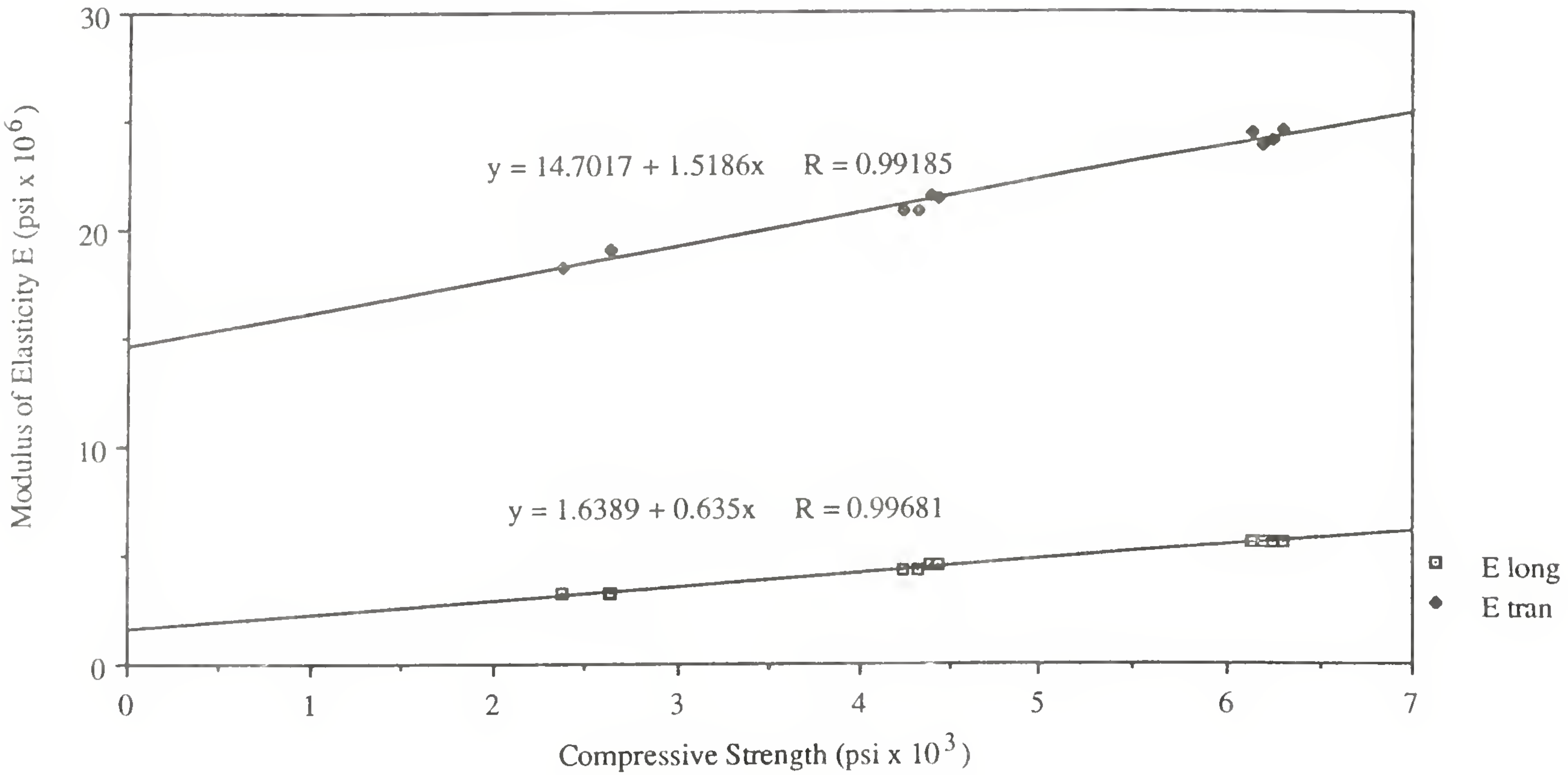

Figure 9.1-1 Correlation between measured values of modulus of elasticity (longitudinal and transverse) and compressive strength.

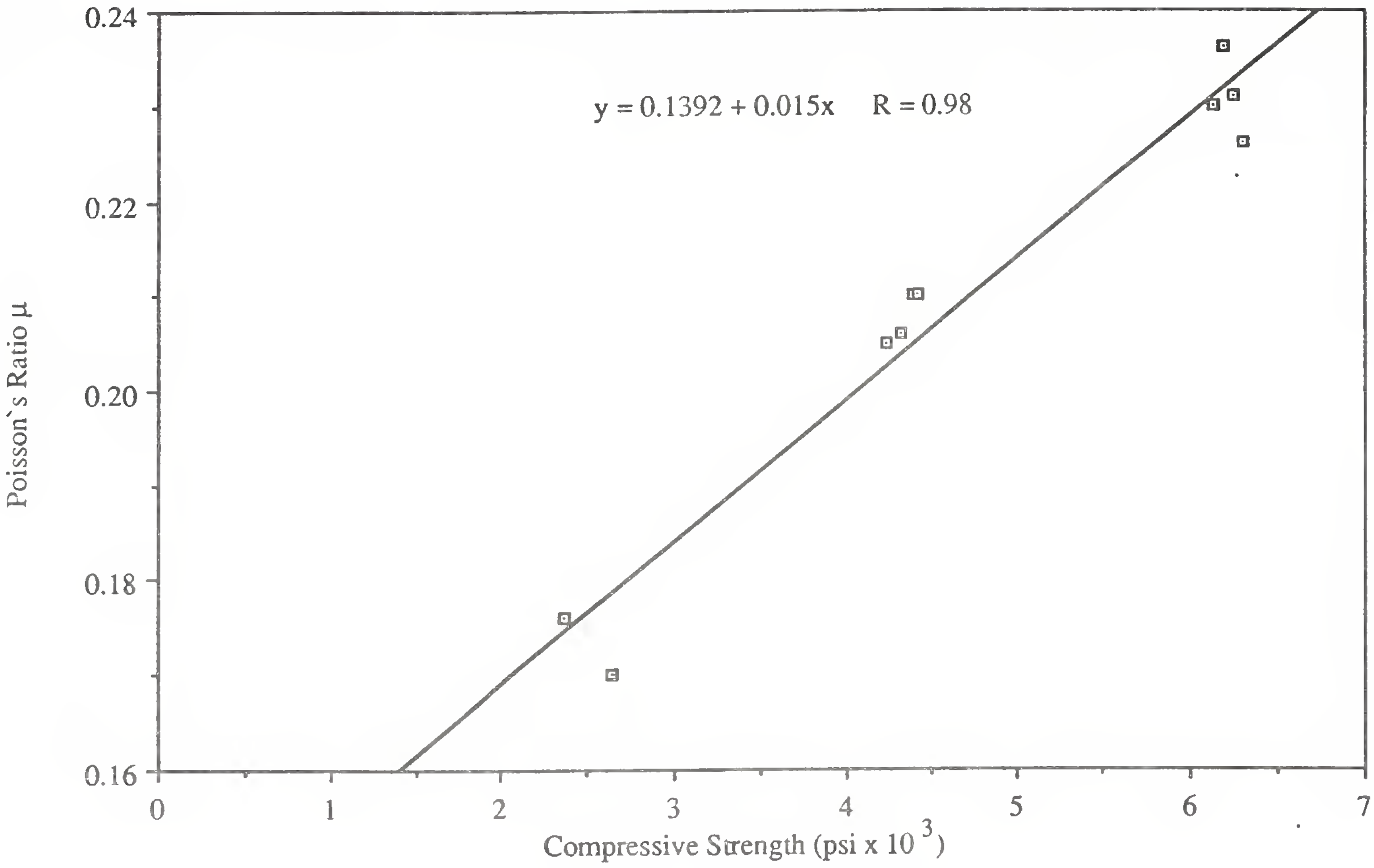

Figure 9.1-2 Correlation between measured values of Poisson's ratio and compressive strength.

Although the data collected in this study are limited, it appears that the values of both modulus of elasticity and Poisson's ratio are very closely and linearly related to the compressive strengths of specimens produced from the same mix. The relationships are presented in Figures 9.1-1 and 9.1-2.

Figure 9.1-1 provides values of longitudinal and transverse modulus of elasticity, each plotted as a function of strength. A linear least-squares regression analysis was performed to derive the best-fitting straight lines, the results of which are given in the figure. The correlation coefficients from this analysis are 0.997 for the relationship between longitudinal (Young's) modulus and strength, and 0.992 for that between the transverse modulus and strength.

As seen in Figure 9.1-1, the slope of the transverse modulus regression line is greater than that of the longitudinal modulus line, indicating that strength increase has a more significant effect on measured values of the transverse modulus than it does on the longitudinal or Young's modulus. However, it should be kept in mind that the values of the transverse modulus are generally about 5 times higher than the corresponding values of the longitudinal modulus, i.e. the axial strains are about 5 times the transverse strains. Actually, on a relative basis the longitudinal modulus is affected more by changes in concrete strength than the transverse modulus.

The correlation between the calculated values of Poisson's ratio and the compressive strength is shown in Figure 9.1-2. Like the elastic modulus, Poisson's ratio increases linearly with strength. As seen from the graph, the linear regression analysis of the data yields a straight line with an R of 0.98.

It was also found that Poisson's ratio increases linearly with Young's modulus. This relationship is shown in Fig. 9.1-3. As indicated in the figure, the same value of R was obtained for this regression as for the relationship between Poisson's ratio and strength shown in Figure 9.1-2.

These findings are based on a relatively small number of observations. Thus the fact that the calculated linear regression coefficients obtained here are so close to 1.0 does not necessarily guarantee that fly ash concrete will always exhibit a close linear relationship between strength and the elastic constants. However, it would be quite useful should such a close relationship be generally established, since it is relatively easy to determine the compressive strength of fly ash concrete and quite difficult to test accurately for elastic modulus and Poisson's ratio. One could derive at least approximate estimates of elastic properties to be expected for any specific fly ash concrete at any age, once its compressive strength - time relationship was established.

The present measured values of Poisson's ratio were also used in the equation for calculating the dynamic modulus of elasticity as discussed subsequently in section 9.2. An increase in Poisson's ratio from 0.170 to 0.236, the range observed in the present results, reduces the calculated value of the dynamic modulus by only about 9%, so that actually the effect of the Poisson's ratio value used is not unduly significant.

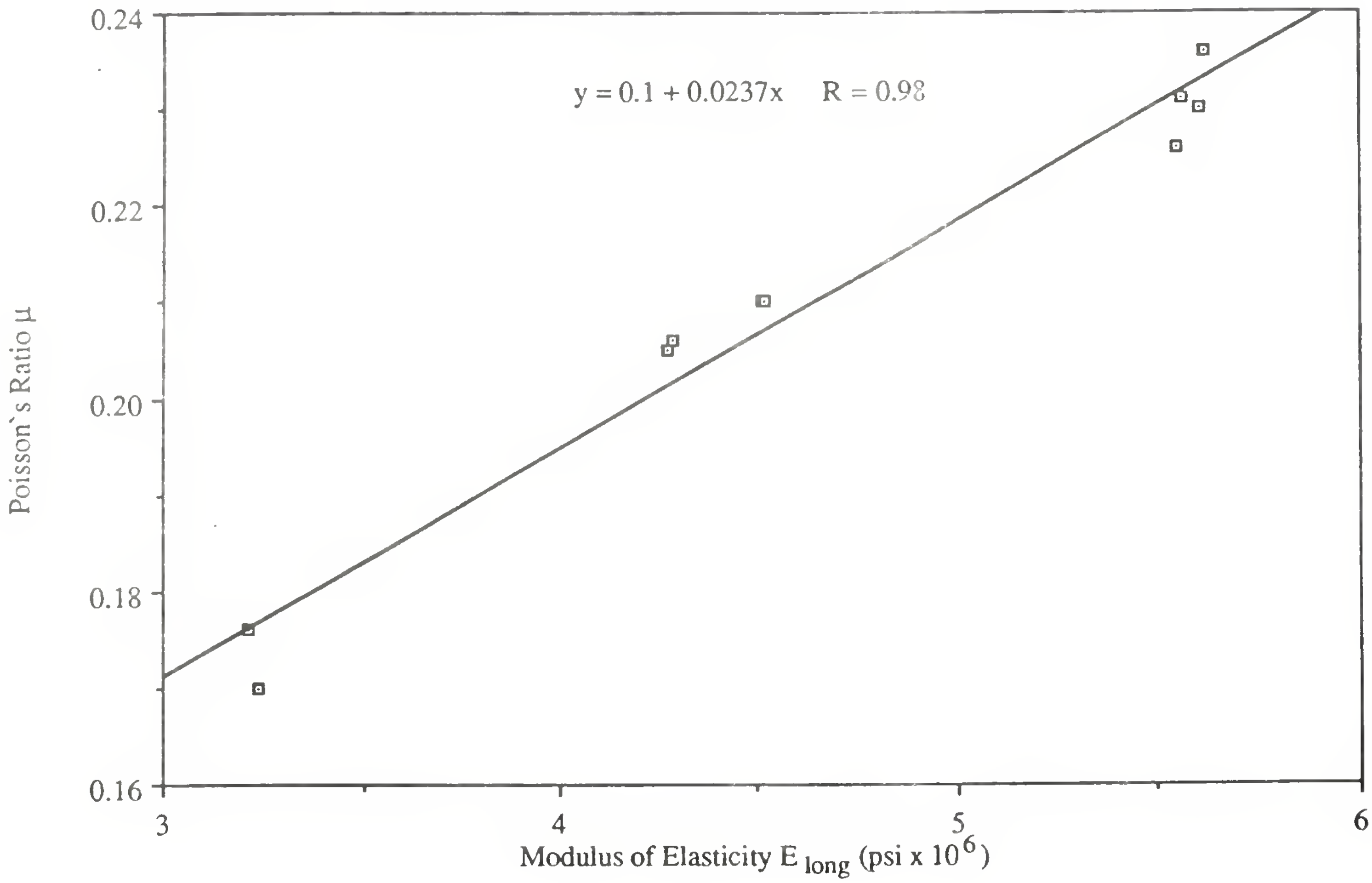

Figure 9.1-3 Correlation between modulus of elasticity and Poisson's ratio.

9.2 Dynamic Modulus of Elasticity

The dynamic modulus of elasticity (E_d) of a number of specimens of fly ash concrete was determined using the pulse velocity method. A portable ultrasonic unit was used to measure pulse velocity as described in Section 4.9.5. The values obtained for E_d are presented in Table 9.2-1 and in Figures 9.2-1 through 9.2-4. Each data point represents the average calculated from determinations on three separate replicate specimens.

The values of the modulus were calculated using the expression

$$E_d = 0.000216\ V^2 p\ [((1+\mu)(1-2\mu))/(1-\mu)]$$

E_d = dynamic modulus of elasticity (psi)
V = longitudinal wave velocity (ft./sec.)
p = density of concrete (lb./ft^3)
μ = Poisson's ratio of concrete

The Poisson's ratio values used were interpolated from the static Poisson's ratio vs. compressive strength relationship described in the preceding section. The density of each concrete specimen was determined from its normal (saturated surface dry) and submerged weights determined at the time of the dynamic modulus measurement.

Table 9.2-1 The dynamic modulus of elasticity E_d of concrete as a function of their composition and curing time.

Mix	E (psi x 10^6) after "c" days					
	c = 1	c = 3	c = 7	c = 28	c = 90	c = 180
L	6.21	6.32	6.41	6.50	6.58	6.65
LF1(15)	5.52	6.30	6.08	6.46	7.06	7.29
LF2(15)	4.79	6.24	6.24	6.35	6.76	6.78
LF3(15)	4.88	5.57	6.22	6.51	6.95	6.78
LC1(15)	5.53	5.94	6.30	6.40	7.16	7.17
LC2(15)	5.67	5.86	6.28	6.77	7.29	7.40
L	6.21	6.32	6.41	6.50	6.58	6.65
LF1(25)	4.90	6.48	5.98	6.66	6.96	7.19
LF2(25)	4.47	5.88	6.24	6.54	6.99	6.76
LF3(25)	4.95	5.85	6.81	6.08	7.07	6.85
LC1(25)	5.21	5.85	6.60	6.77	7.05	6.99
LC2(25)	5.45	6.29	6.06	6.92	7.24	7.12
S	5.05	5.83	5.80	6.48	6.90	6.96
SF1(15)	4.64	5.78	6.04	6.62	7.24	7.31
SF2(15)	5.36	5.82	5.92	6.51	6.54	6.54
SF3(15)	5.36	5.69	6.36	6.46	6.87	7.16
SC1(15)	5.41	5.76	6.20	6.44	6.95	6.86
SC2(15)	5.74	5.99	6.08	6.55	7.03	6.96
S	5.05	5.83	5.80	6.48	6.90	6.96
SF1(25)	4.52	5.82	5.63	6.21	6.89	7.18
SF2(25)	4.71	5.73	5.94	6.70	6.80	6.94
SF3(25)	5.15	6.14	6.73	6.89	6.90	6.54
SC1(25)	4.97	6.04	5.76	6.49	6.53	6.83
SC2(25)	5.18	5.78	6.35	7.05	6.89	7.12

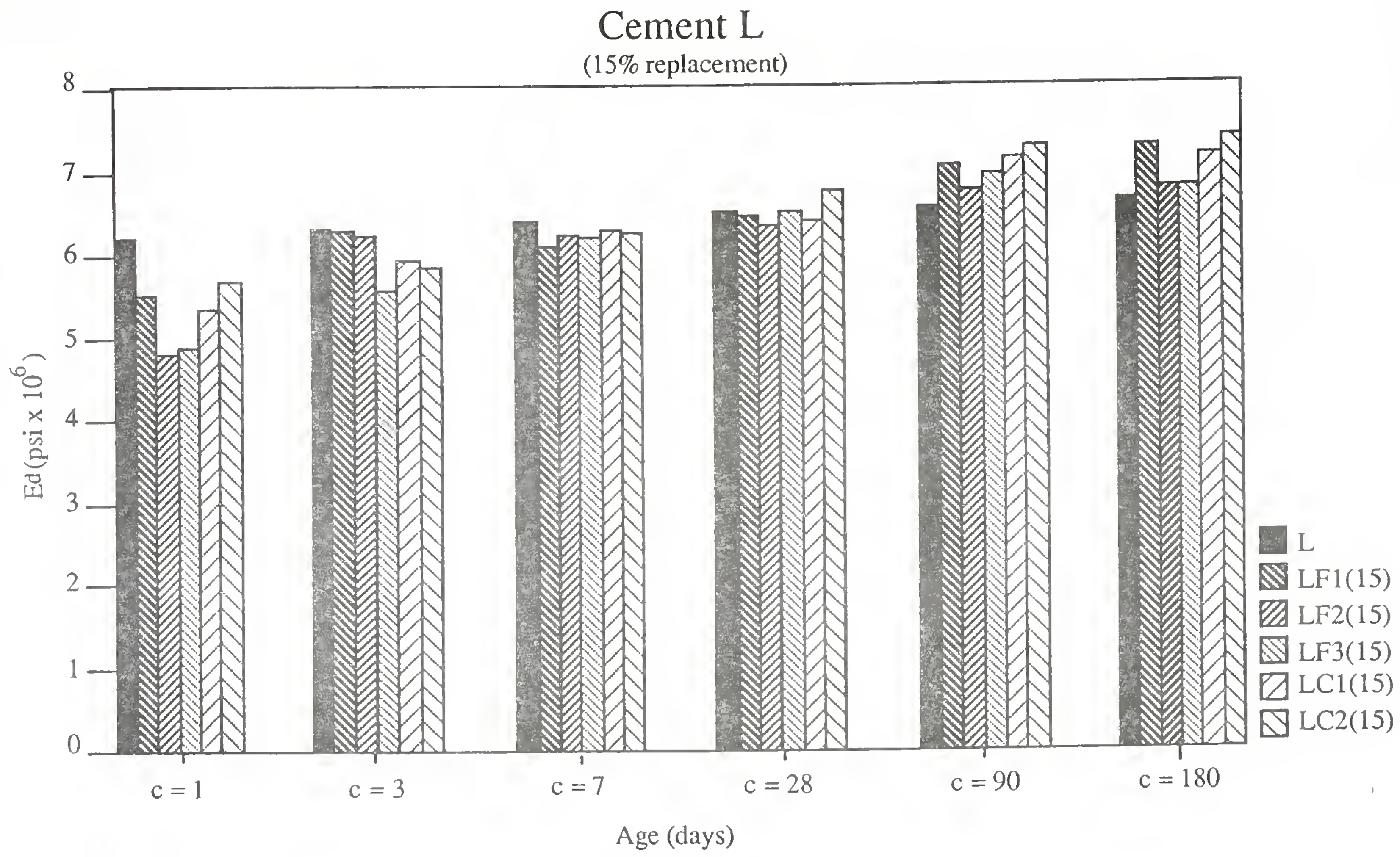

Figure 9.2-1 Dynamic modulus of elasticity of plain and fly ash concretes moist cured for a "c" days, (cement L, 15% replacement).

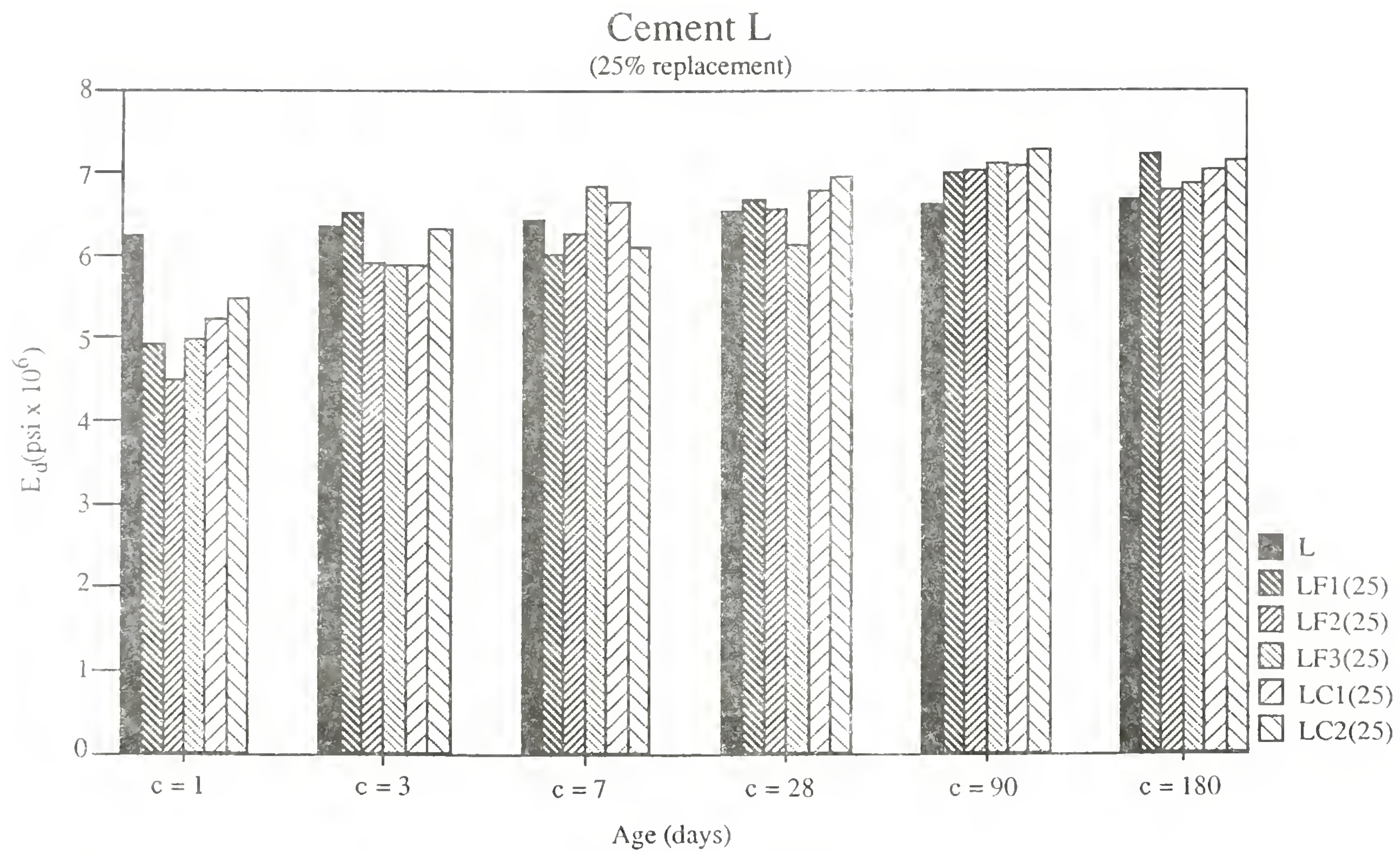

Figure 9.2-2 Dynamic modulus of elasticity of plain and fly ash concretes moist cured for a "c" days, (cement L, 25% replacement).

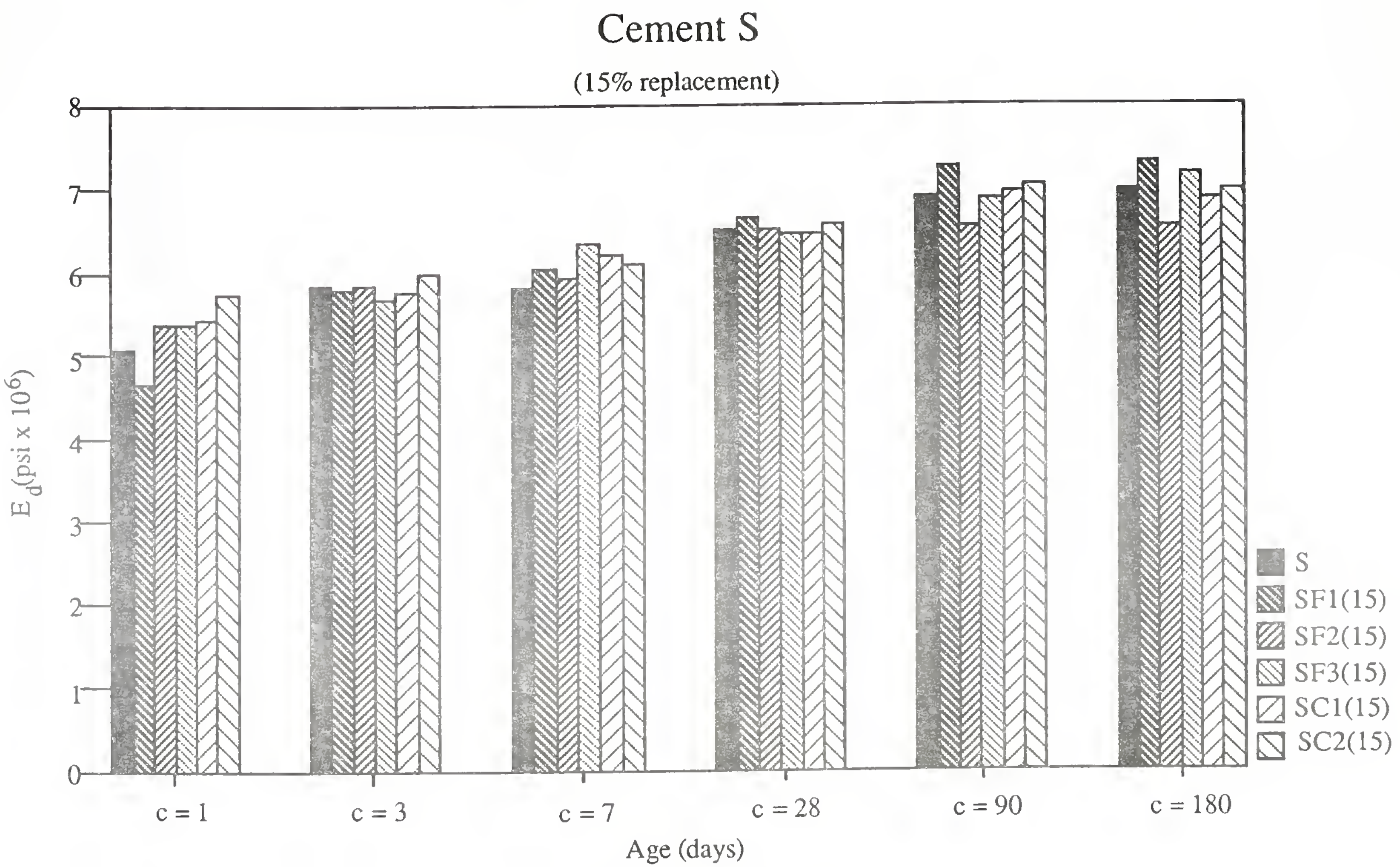

Figure 9.2-3 Dynamic modulus of elasticity of plain and fly ash concretes moist cured for a "c" days, (cement S, 15% replacement).

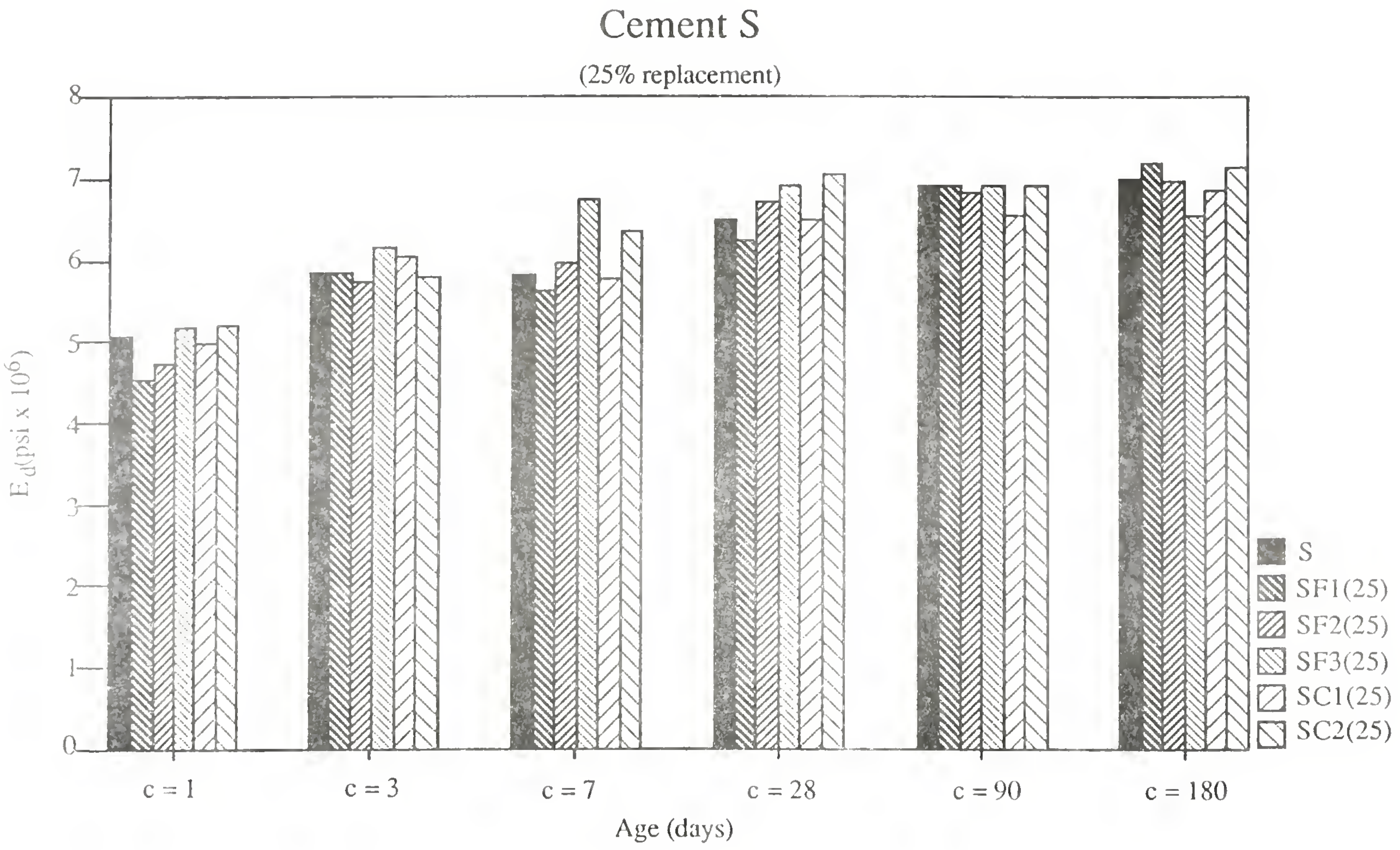

Figure 9.2-4 Dynamic modulus of elasticity of plain and fly ash concretes moist cured for a "c" days, (cement S, 25% replacement).

The effects of the individual fly ash, cement, and curing period used on the E_d can be seen in the graphs provided.

It was found that the E_d values for plain cement concretes at a given age were different for the two cement used. As will be shown subsequently in Section 9.3, cement L produced concretes of higher compressive strengths. The 1-day E_d value for plain concrete with this cement was unexpectedly high, 6.2 x 10^6 psi. However, the increase in E_d with time was only moderate, the value attained at 180 days being 6.65 x 10^6 psi, only 7% higher.

In contrast, the pattern of development of the dynamic modulus in plain cement concrete was very different with cement S, which produced concretes of lower compressive strength. The 1-day value of E_d was only 5.05 x 10^6 psi, 33% lower than that with cement L. However, with cement S, E_d increases rapidly with time. At 180 days it reaches a value of 6.96 x 10^6 psi which is actually 5% higher than that of the cement "L" plain concrete at the same age. The increase in dynamic modulus between 1 day and 6 months was about 38% for this concrete, a major increase.

These differing patterns of E_d development over time experienced by the plain concretes are not visible in the behavior of the fly ash concretes made with the two cements. For example, it can be seen from comparison of Figures 9.2-1 and 9.2-3 that at a 15% replacement level, the 1-day values of E_d for fly ash concrete fall roughly in the range between 4.7 and 5.7 x 10^6 psi, and the 180-day values are in the range between about 6.8 and 7.4 x 10^6 psi irrespective of the cement used. Thus the effect of the cement itself seems to have been overpowered by the incorporation of fly ash, at least with respect to the pattern of increase in E_d. Similar behavior is also observed for the 25% replacement level (Figures 9.2-2 and 9.2-4).

It appears from the data for fly ash concretes that the pattern of development of E_d is strongly affected by the individual fly ash used, rather than by the cement used.

In virtually every case, irrespective of the particular cement and the fly ash replacement level used, the 1-day values of E_d were highest for concretes containing high calcium fly ash C2. At the same age, the lowest E_d values were usually associated with one of the low calcium fly ashes.

The extension of curing time up to 6 months modifies the above trends only slightly. While concretes containing C2 fly ash continue to maintain high E_d values throughout the entire testing period, similar high values were also developed at ages of 90 days or more in concretes containing the low calcium fly ash F1.

Except for this specific fly ash, the comparative results for the different fly ashes after extended curing resemble those at 1 day; the lowest values of E_d continue to be associated with the F2 and F3 low calcium fly ashes.

These results indicate that fly ash significantly influences the elastic properties of concrete as measured by dynamic modulus of elasticity, even at replacement levels as small as 15%. This indication might be of special interest in prestressed structures, where use of fly ash might even help in reducing prestress loss for concretes which contain cements that behave like cement S.

Another observation based on analysis of the data of Figures 9.2-1 through 9.2-4 is that the values of E_d for fly ash concretes, while initially lower, can match or exceed those for similar plain concretes at ages above 28 days.

It is generally understood that static and dynamic measures of the modulus of elasticity of concrete measure quite different things. However, it is of interest to compare them for fly ash concretes since such information is generally not available.

Since both sets of measurement are so strongly affected by compressive strength, it seems most appropriate to compare them at equal compressive strength values. To make such comparisons, corresponding data were extracted from Tables 9.1-1 and 9.2-1 respectively, and compiled in Table 9.2-2.

Table 9.2-2 The values of dynamic modulus of elasticity E_d and static modulus of elasticity E_l of fly ash concretes as a function of compressive strength level.

Compressive strength (psi)	E_d (1×10^6 psi)	E_1 (1×10^6 psi)	Relative difference (%)	E_1/E_d
2000	5.0	3.2	56	0.64
4000	6.2	4.3	44	0.69
6000	7.0	5.5	27	0.78

The data of Table 9.2-2 reveal that, as expected, at any given strength level, the dynamic modulus of elasticity E_d is appreciably higher than the corresponding static modulus of elasticity E_{long}.

The percentage difference between the E_d and E_l values was quite high, over 50%, at the lower compressive strength levels characteristic for fly ash concretes at early ages.

This difference reduces for more mature concretes and after 6 months of curing drops to about 30%. Differences of this order are commonly reported for plain concretes. The dynamic modulus of plain concrete is commonly observed to be 20% to 30% higher than the static modulus, depending on the strength of concrete. It should be recalled that the dynamic modulus is determined at very low stress levels and is therefor probably more representative of the actual elastic behavior of the material, i.e. the effect of creep is negligible.

The generally higher percentage differences reported here, especially for young fly ash - bearing concretes, can most likely be attributed to the differences in moisture content of samples tested. The static modulus of elasticity E_l was tested on an air-dry samples; in contrast, the dynamic modulus E_d was tested on samples in the saturated surface dry condition, as is normally done. Since the pulse velocity method of E_d determination is known to be particularly sensitive to changes in sample moisture content, it seems likely that much of the observed high percentage differences observed can be attributed to the high water content in the young samples being tested rather than to the any particular fly ash effect.

The data presented in Table 9.2-2 also show that, similarly to what is observed in plain concretes, the ratio of the static to dynamic moduli increases with concrete strength. This indicates that while the incorporation of fly ash may change the actual values of the static and dynamic moduli as compared with those of plain concrete, it seems not to influence the general pattern of elastic behavior of the material.

9.3 Measurements of Concrete Strength

A detailed analysis and discussion of all strength results obtained during this study is presented in this section. The section is divided into two parts, one containing a general description of the ranges of measured strengths and their changes with time, the other describing the variations in strength response for the two specific cements and the five fly ashes used in this project. Measurements of both compressive and flexural strengths are discussed together.

9.3.1 General Characterization of Strength

One of the objectives of this study was to establish whether "constant paste quality" concrete designed by the suggested procedure for a variety of fly ashes would achieve strengths comparable with those of equivalent plain concretes, and at what ages such equivalent strengths might be attained.

Accordingly, compressive and flexural strengths tests were carried out for all of the concretes after 1, 3, 7, 28, 90 and 180 days of moist curing. Summaries of the test results are presented in Tables 9.3-1 for compressive strengths and 9.3-2 for flexural strengths. Each value in these tables represents the average of results for three individual samples. The same results are presented graphically in

Figures 9.3-1 through 9.3-4 for compressive strength and in Figures 9.3-5 through 9.3-8 for flexural strength.

In each of the figures the strength of the reference plain concrete is displayed with a heavy trend line to facilitate the comparisons.

Table 9.3-1 Summary of compressive strength values for concretes with and without fly ash.

Mix	Compressive strength (psi) tested after:					
	1 day	3 days	7 days	28 days	90 days	180 days
L	2214	3310	4022	5553	6413	7017
LF1(15)	2196	3133	3599	5223	6395	7184
LF2(15)	1584	3427	3916	5352	6213	6183
LF3(15)	1884	3033	4099	5053	6137	6313
LC1(15)	1996	3215	3916	5129	6154	6926
LC2(15)	2509	3080	4281	5771	6113	7220
LF1(25)	1997	3216	3969	5118	6643	6696
LF2(25)	1343	2738	4000	4405	6048	6007
LF3(25)	1684	2703	3734	4629	6366	6525
LC1(25)	1843	3015	4858	5930	6702	7185
LC2(25)	1955	3021	4052	5748	7161	6784
S	2138	3410	3680	5053	5477	6160
SF1(15)	1773	2715	3587	5094	6054	6342
SF2(15)	1832	2797	3457	4823	5954	6136
SF3(15)	2120	2627	3586	4640	6790	6878
SC1(15)	1867	3021	3834	5318	6513	7208
SC2(15)	2355	3263	3769	5795	6807	7079
SF1(25)	1307	2709	2898	4294	5924	6513
SF2(25)	1572	2756	3162	4443	5171	6537
SF3(25)	1602	2833	3657	4546	5813	6107
SC1(25)	1926	3168	3496	5154	5292	6737
SC2(25)	1449	2621	3875	5819	6543	6692

Table 9.3-2 Summary of flexural strength values for concretes with and without fly ash.

Mix	Flexural strength (psi) tested after:					
	1 day	3 days	7 days	28 days	90 days	180 days
L	400	661	874	942	941	905
LF1(15)	435	576	598	738	888	936
LF2(15)	346	601	655	832	863	861
LF3(15)	374	513	638	832	887	877
LC1(15)	405	462	678	775	880	925
LC2(15)	453	583	725	900	943	940
LF1(25)	421	557	590	711	903	888
LF2(25)	279	524	633	708	919	845
LF3(25)	380	483	585	703	840	862
LC1(25)	331	516	640	825	903	883
LC2(25)	442	630	691	766	911	902
S	414	607	687	838	854	901
SF1(15)	365	547	658	784	903	893
SF2(15)	443	550	606	856	860	834
SF3(15)	427	547	675	844	932	992
SC1(15)	462	534	684	823	865	872
SC2(15)	466	658	647	847	939	956
SF1(25)	288	508	494	787	827	929
SF2(25)	344	564	560	681	858	866
SF3(25)	332	515	686	760	809	874
SC1(25)	354	571	576	736	785	864
SC2(25)	361	505	653	799	849	893

It is apparent from Figures 9.3-1 to 9.3-4 that the fly ash concretes examined here attain generally similar compressive strengths to those attained by the reference plain concrete at all ages. The band containing the data is somewhat narrower for the 15% replacement level than for the 25% level, as might be expected; at a higher level, differences in inherent strength gain potential among the different fly

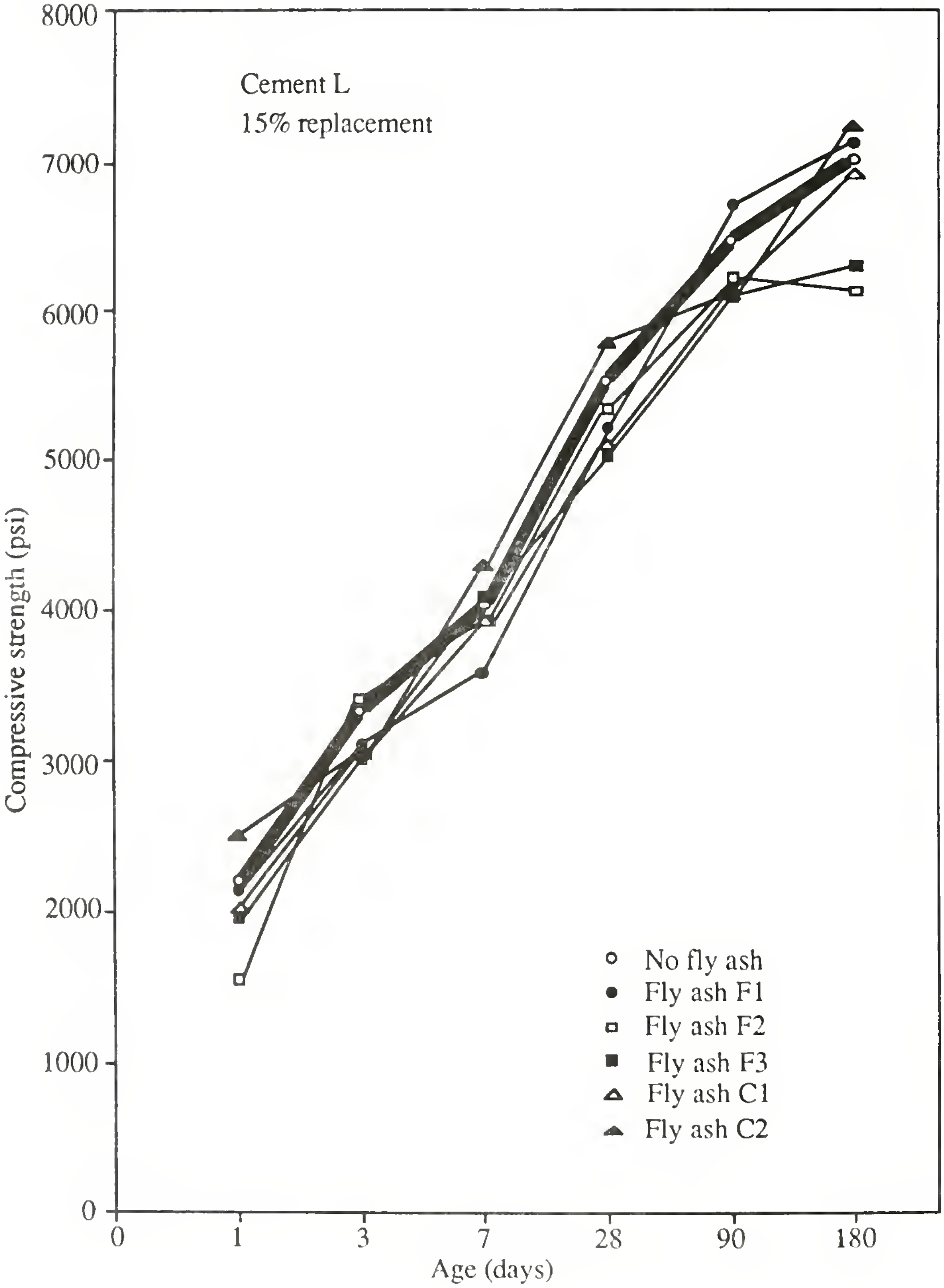

Figure 9.3-1 Compressive strength development with time of plain and fly ash concretes (cement L, 15% replacement).

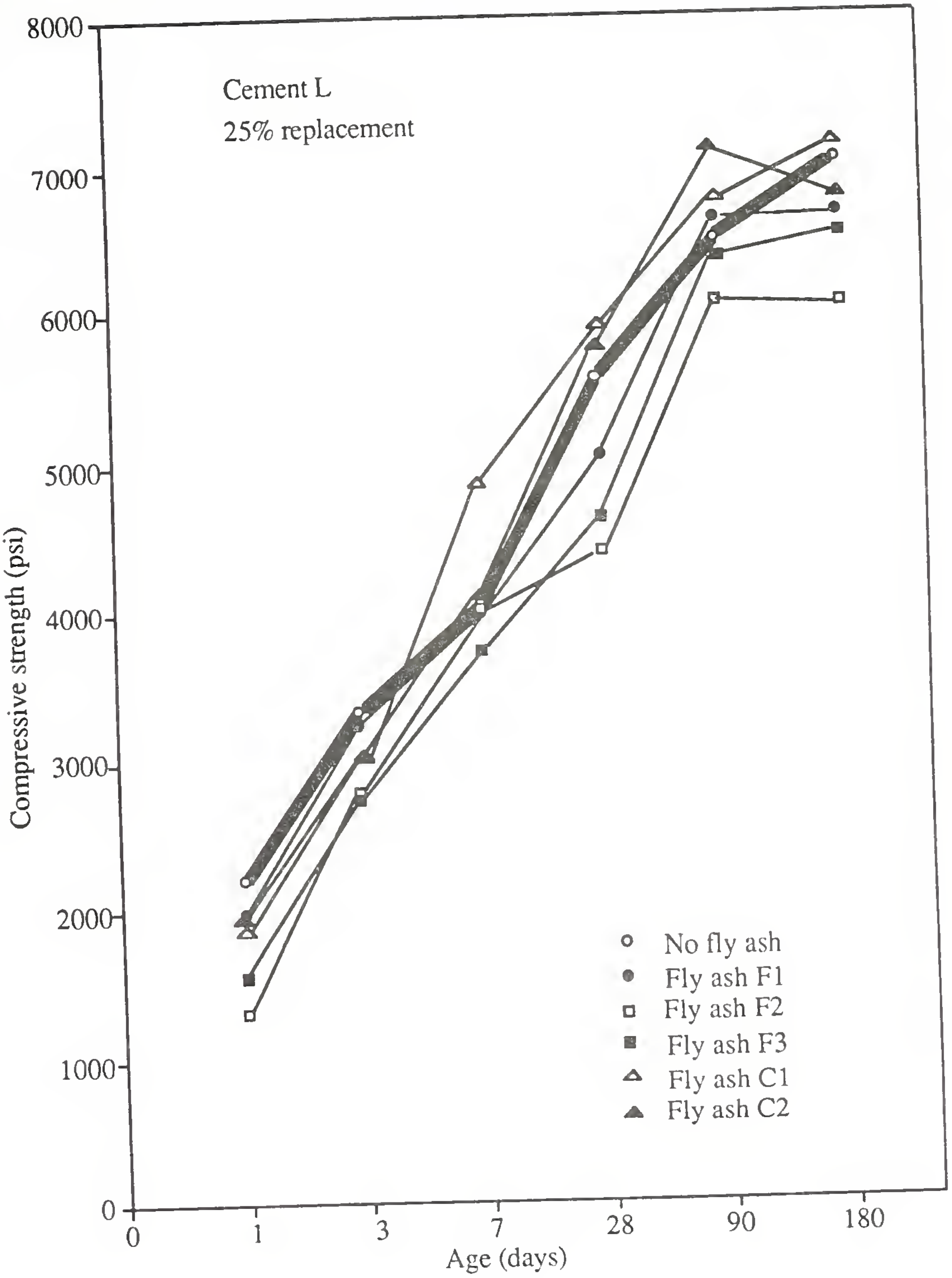

Figure 9.3-2 Compressive strength development with time of plain and fly ash concretes (cement L, 25% replacement).

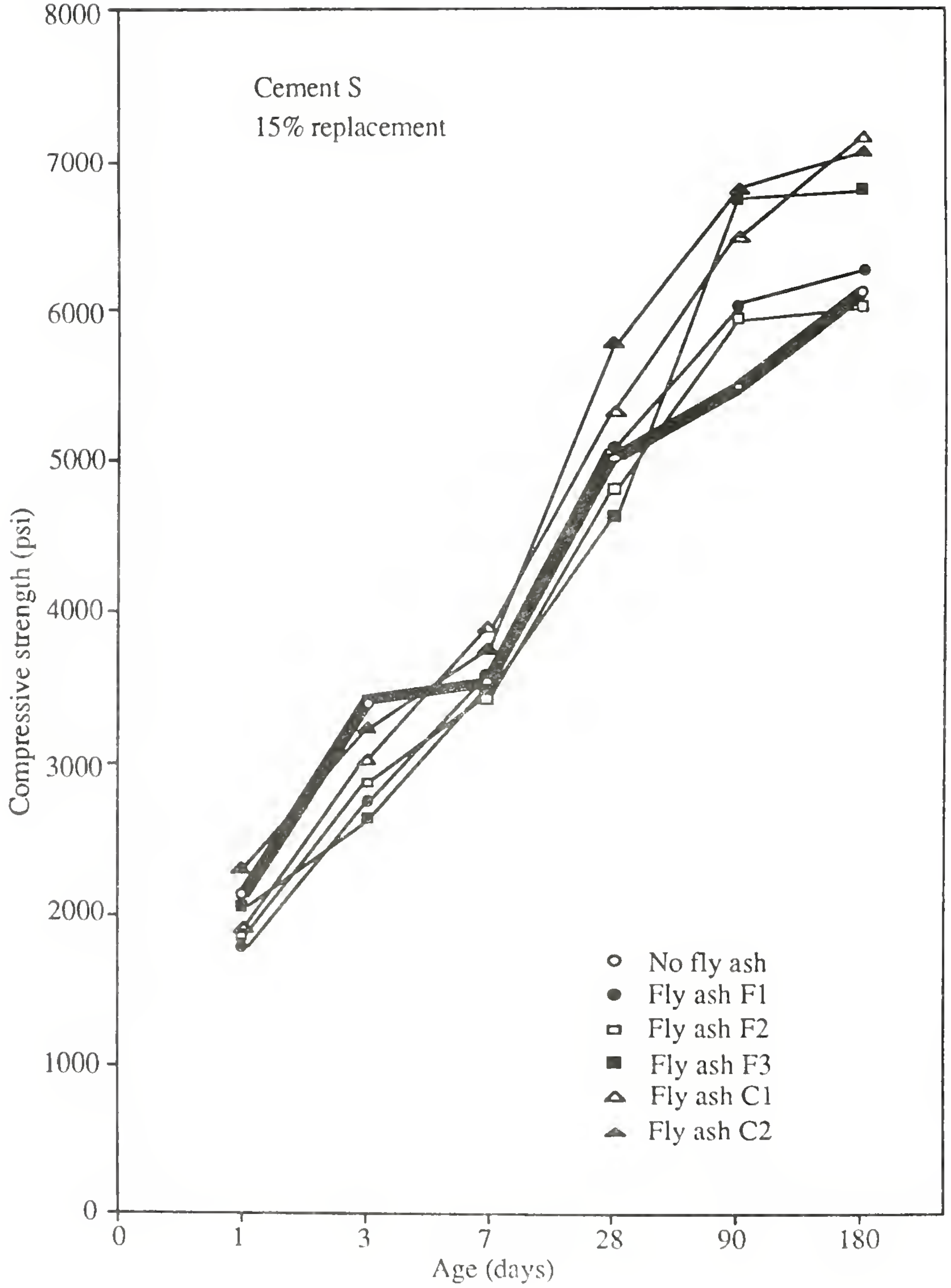

Figure 9.3-3 Compressive strength development with time of plain and fly ash concretes (cement S, 15% replacement).

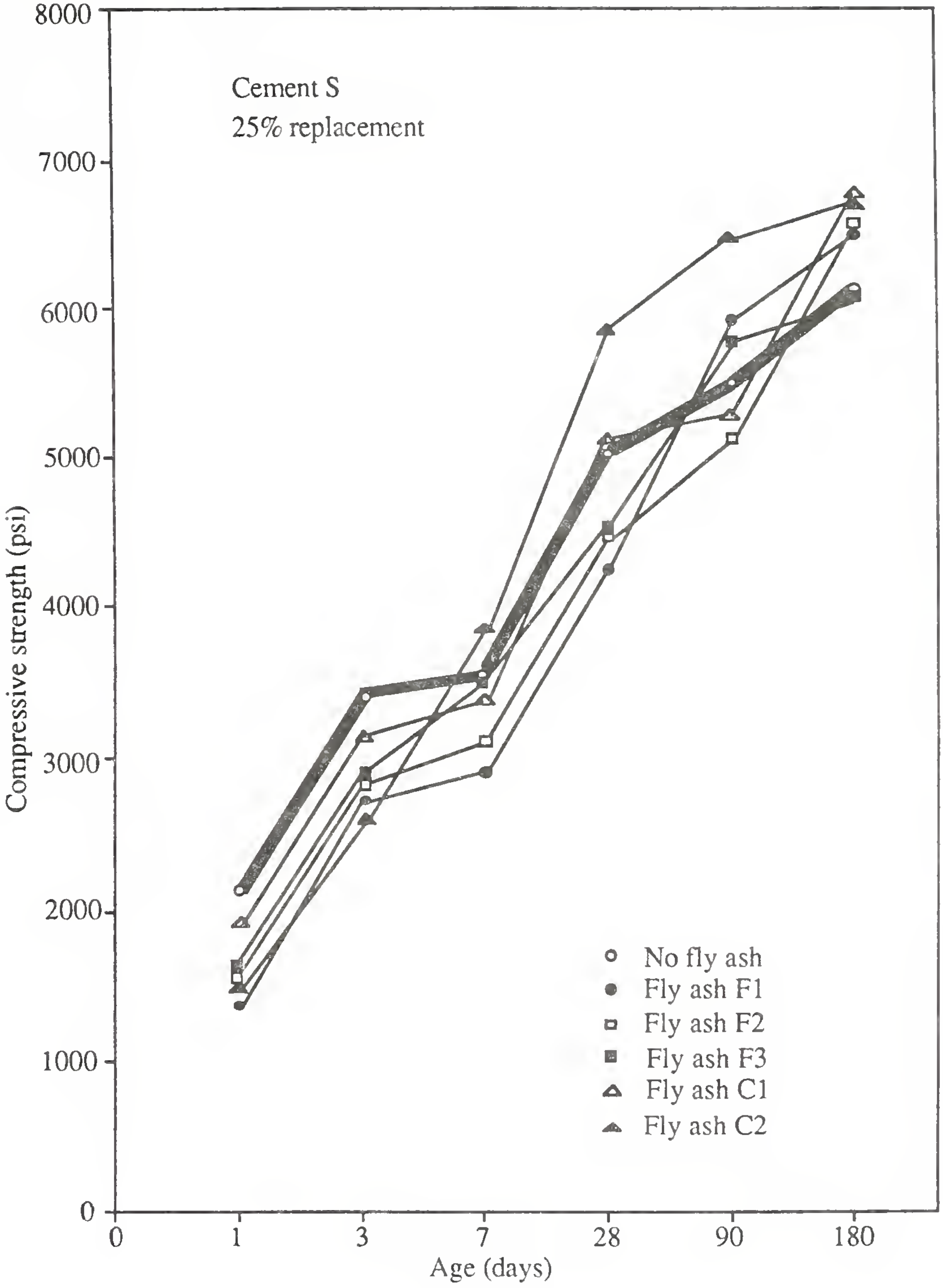

Figure 9.3-4 Compressive strength development with time of plain and fly ash concretes (cement S, 25% replacement).

ashes have more pronounced effects.

Also as might be expected, at the 25% replacement level the fly ash concretes did not quite match the strength of the reference concretes at 1 day or 3 days. Of course, where this early strength development is important, one could readily insure it by selecting a lower w:(c+fa) ratio.

The graphs in Figures 9.3-2 and 9.3-4 also indicate even at 28 days, using low calcium fly ashes at the 25% replacement level might have some impact on compressive strength. At this age, concretes containing 25% of the F1 and F2 fly ashes developed compressive strengths about 600 psi (11%) to 1000 psi (18%) lower than the corresponding plain concrete, depending on the cement used. As indicated in Table 3.2-1, both of these fly ashes contain substantial contents of magnetic particles, which are primarily composed of relatively unreactive iron oxides. Both also contain high contents of particles coarser than 45 µm, which are also relatively unreactive with cement. Thus, the low 28 day compressive strength can be explained by the intrinsic character of these fly ashes.

Subsequent strength development does lead to satisfactory strengths at later ages with these fly ashes, as seen in Figures 9.3-2 and 9.3-4.

If such fly ashes are to be used, and the concretes are required to meet a specified 28-day strength minimum, a lower w:(c+fa) ratio should be selected or the replacement level should be reduced.

In general, for ages less than 60 days the low compressive strengths of concretes containing 25% of F1 and F2 fly ashes seems to be independent of the cement used. We believe that this is explainable on the basis that a sufficient extent of pozzolanic reaction has not yet taken place by this time. As the pozzolanic reaction progresses, the situation changes, and the importance of the type of cement used becomes more apparent. This will be discussed further in the next section.

Finally, it should be noticed that for curing times longer than 90 days, in the cases where fly ash concretes are weaker than the reference concretes, they are only a few hundred psi weaker. In many cases by 90 days the fly ash concretes achieved compressive strength values considerably higher than those of the corresponding plain concretes.

The effects of fly ash on the development of flexural strength are somewhat different than for compressive strength.

Analysis of Figures 9.3-5 to 9.3-8 reveals two important facts related to flexural strength. First, it is observed that for virtually all ages, all of the fly ash concretes tested (except for a few mixes made with cement S at 15% replacement level) developed lower flexural strength than did the reference concretes.

The biggest differences between the flexural strength of the reference and fly ash concretes were observed after 7 and 28 days of curing. For example at 7 days the values of flexural strength were all substantially lower than those of the reference concrete, by about 20% for the high calcium fly ashes, and by about 33% for the low calcium fly ashes.

In concretes based on cement S, significantly lower flexural

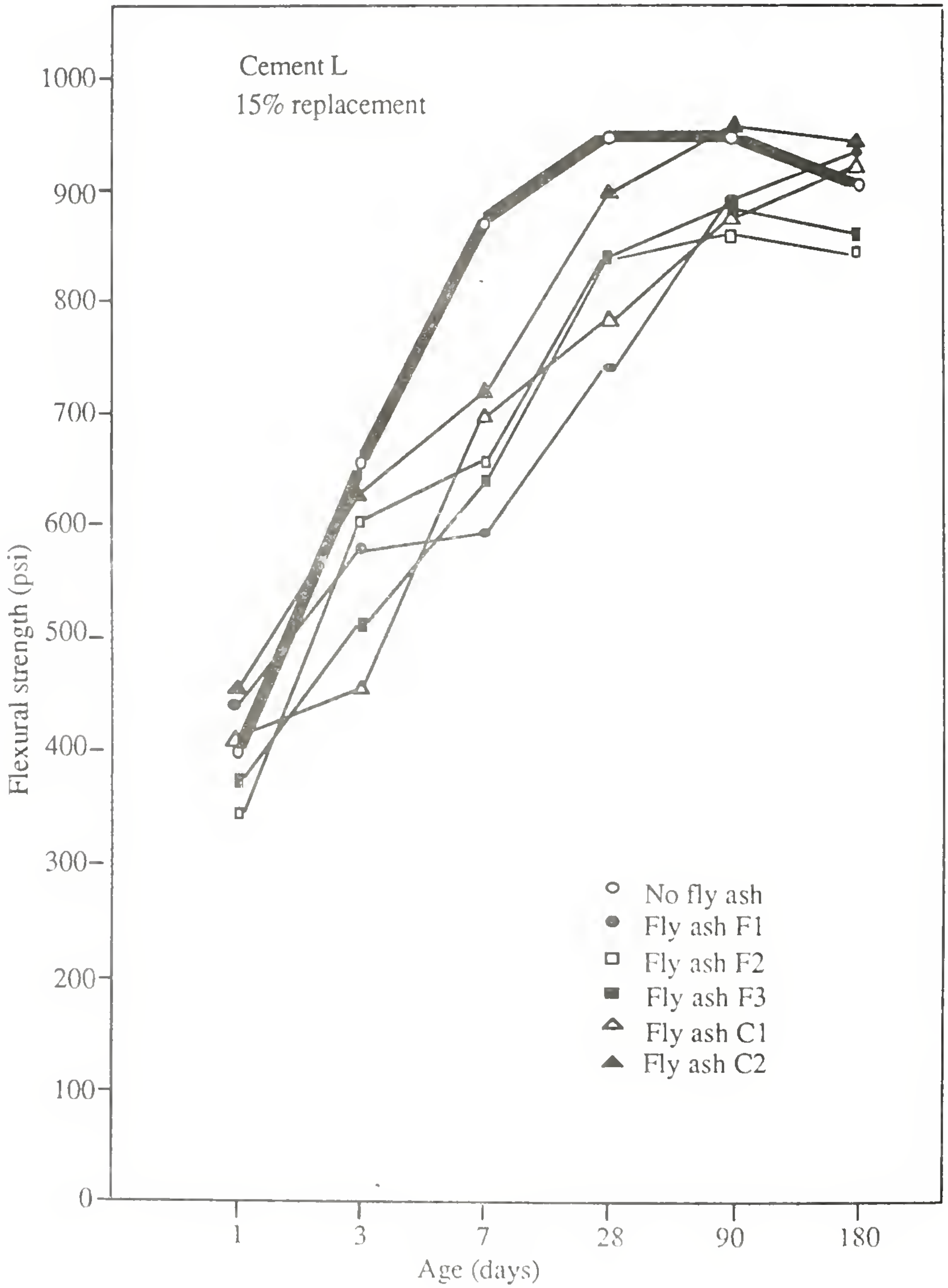

Figure 9.3-5 Flexural strength development with time of plain and fly ash concretes (cement L, 15% replacement).

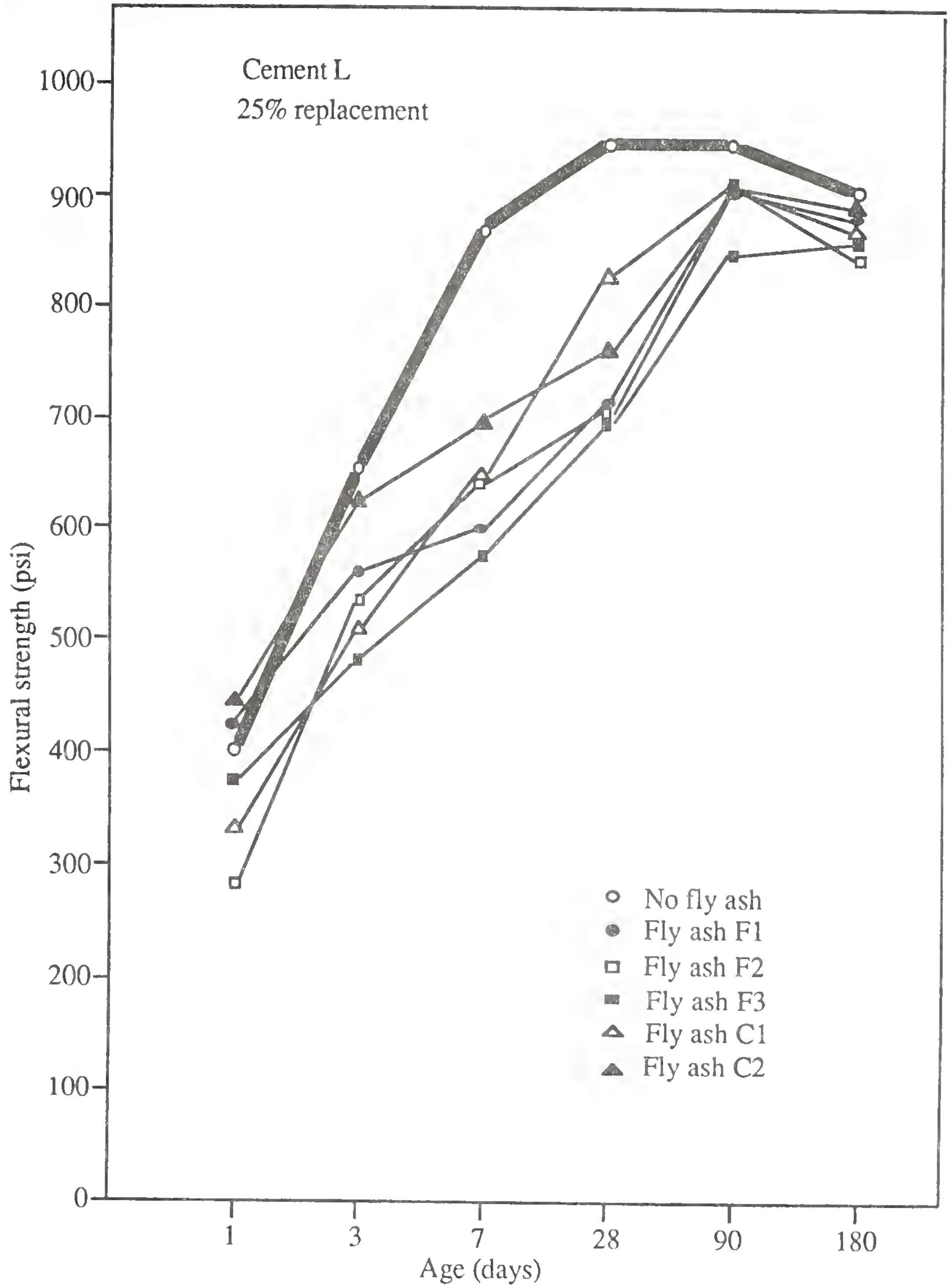

Figure 9.3-6 Flexural strength development with time of plain and fly ash concretes (cement L, 25% replacement).

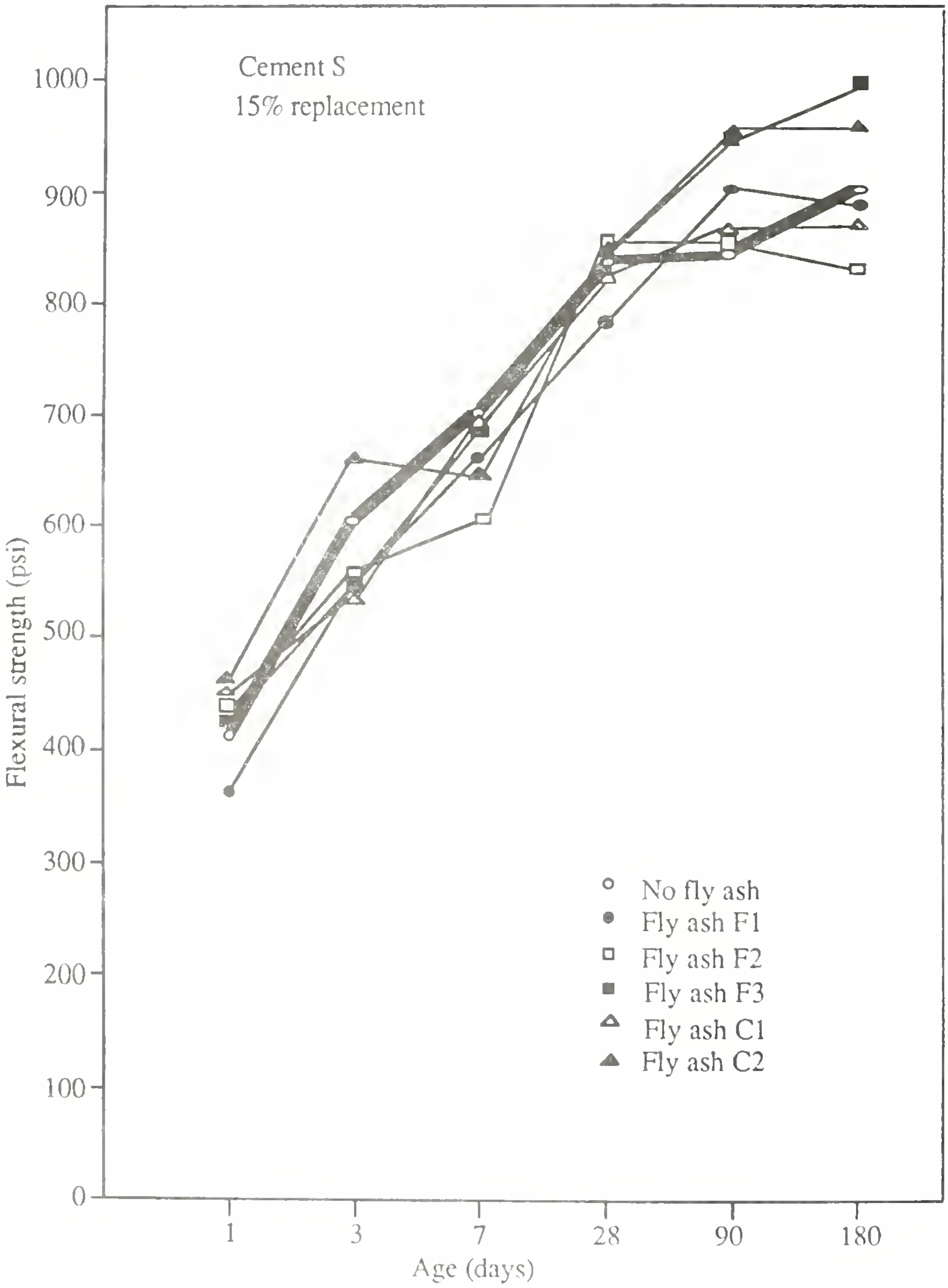

Figure 9.3-7 Flexural strength development with time of plain and fly ash concretes (cement S, 15% replacement).

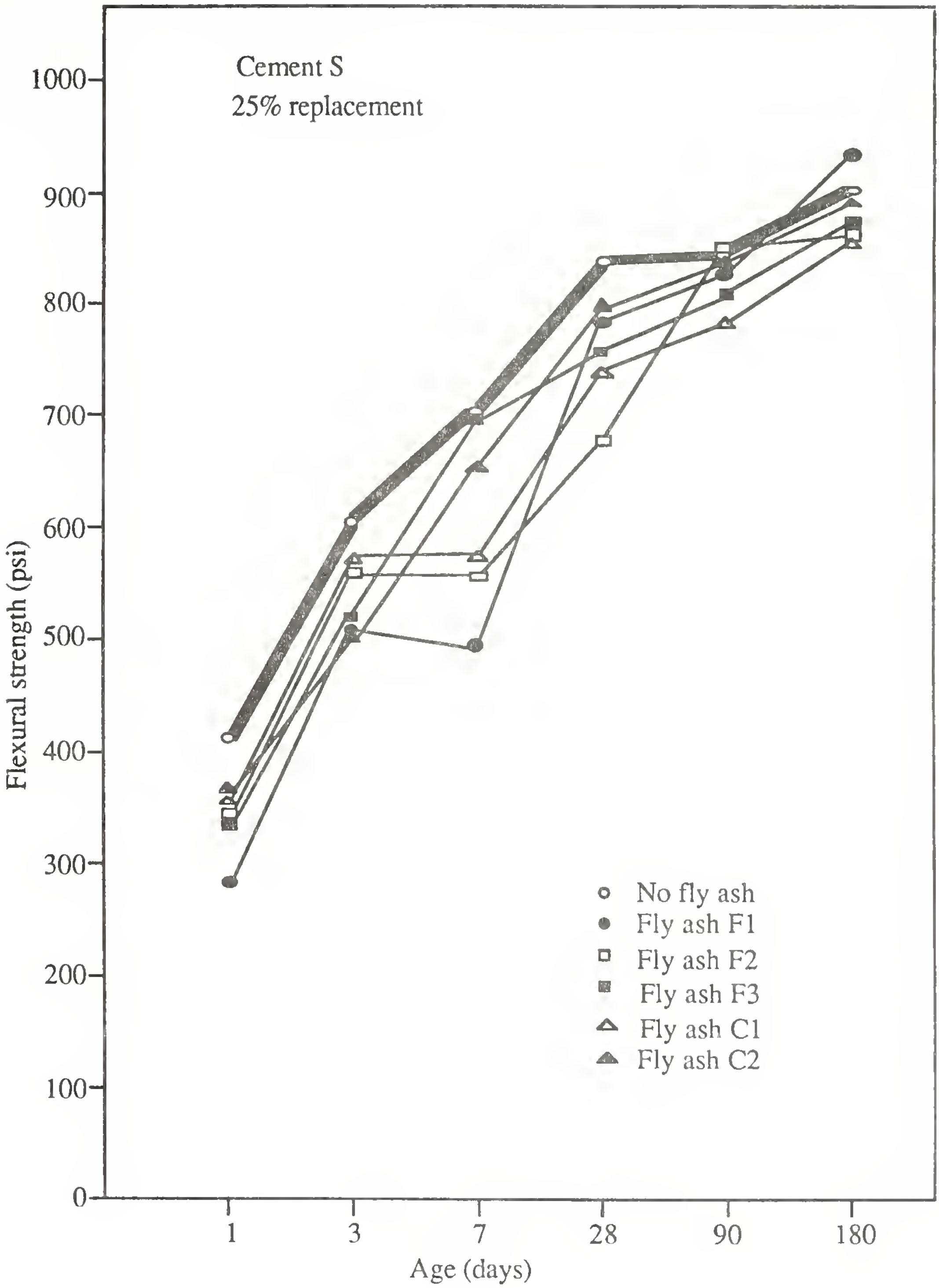

Figure 9.3-8 Flexural strength development with time of plain and fly ash concretes (cement S, 25% replacement).

strengths occurred only at the 25% replacement level, with the maximum difference being 28%, observed for fly ash F1 at 7 days. Since, as discussed previously, only occasional and relatively small differences between compressive strengths of reference and fly ash concretes were found, it appears that fly ash addition tends to negatively influence flexural strength more than it does compressive strength. This observation might be of practical significance, and it suggests that the relation between compressive and flexural strength in a fly ash concrete may be different in character from that existing in plain concrete.

Secondly, the effect of the specific cement used is pronounced for plain concrete but not for fly ash concretes. Nor do the different fly ashes exert much influence; in flexure there seems to be comparatively little difference among the results obtained with the different fly ashes. From the practical point of view, for either of the two replacement levels used, all of the flexural strength data fall within the same range, regardless of the specific cement or fly ash used.

In general, the data presented here indicate that the CPQ mix design method can be successfully used to proportion fly ash concretes of appropriate compressive strength range, regardless of the fly ash used, and regardless of the fact that this method does not focus on strength as a parameter. Despite the intentional variations in the type of fly ash, the cement, or the replacement level used, in most cases the compressive strengths of the fly ash concretes were similar to or better than that of the corresponding plain concrete.

The effect of fly ash on flexural strength is somewhat less favorable. Evaluating the factors involved is complicated by the fact that, as discussed earlier, changing the type of cement may have a more pronounced effect on the flexural strength development of plain concrete than substituting fly ash does.

The general trend observed for flexural strength data seems to be that use of fly ash will result in some flexural strength reduction. The results show that this reduction is more severe when using the more reactive cement L, than it is when using less reactive cement S.

The actual values of flexural strength for the fly ash concretes at a given age tend to be grouped in a relatively narrow range, virtually irrespective of the cement used. For concretes cured for 90 days or longer, the flexural strengths approach, or in some case surpass, those of plain reference concretes.

9.3.2 Effect of Cement and of Replacement Level

Figures 9.3-1 to 9.3-8 presented in the previous section were aimed at showing the general trends in the development of strength of fly ash concrete with time, and were focused on comparisons of strength development exhibited by fly ash concretes vs. those of plain reference concretes. Such comparison allows for a broad assessment of the influence of fly ash on strength.

In this section we provide a more detailed analysis of the compressive and flexural strength results for all of the concrete batched with a given fly ash. The focus here is on the effect of (a) the particular cement, and (b) the replacement level, on strength development in concrete batched with a given fly ash.

Figure 9.3-9 compares compressive strengths development for plain reference concretes made with cement L and cement S respectively. For up to 3 days, there was no significant difference. Beyond 3 days, the cement L concretes gained strength at a significantly faster rate than did the cement S concretes.

This trend continued up to 90 days, at which time concretes made with cement L reached a compressive strength of 6400 psi, about 1000 psi (17%) higher than those made with cement S. After 90 days, the rate of strength development for cement L concretes slowed, and at 180 days the difference between cement L concretes and cement S concretes was the same 17% observed at 90 days.

The somewhat higher activity of cement L may also be seen in Figures 9.3-10 to 9.3-14, which contain graphs showing the strength development of fly ash concretes. Each figure describes results for a different fly ash. Each contains a set of four graphs; two give the strength-time relationship for the 15% and 25% replacement levels in concretes based on cement L, the other two giving the same information for concretes based on cement S.

Although the differences are usually not very significant, fly ash concretes made with cement L tend to have slightly higher strengths than their companions made with cement S.

The higher activity of a cement L is probably also responsible for another trend displayed by the concretes analyzed during this research program. It can be seen from the graphs that for a short curing periods (3 to 7 days), the strengths of cement L concretes at the 15% fly ash replacement level are usually higher than those at the

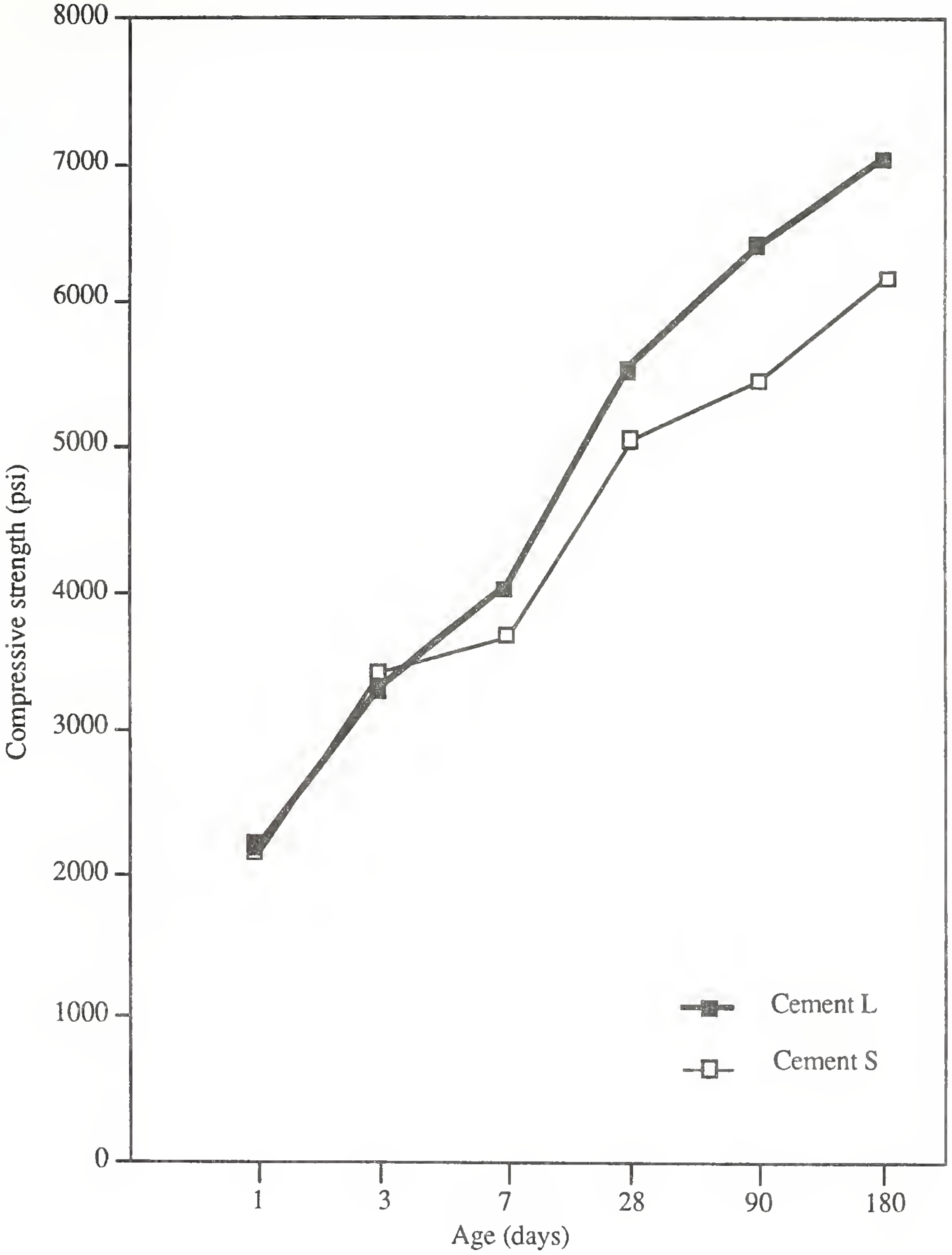

Figure 9.3-9 The compressive strength-curing time relationship for a plain concrete.

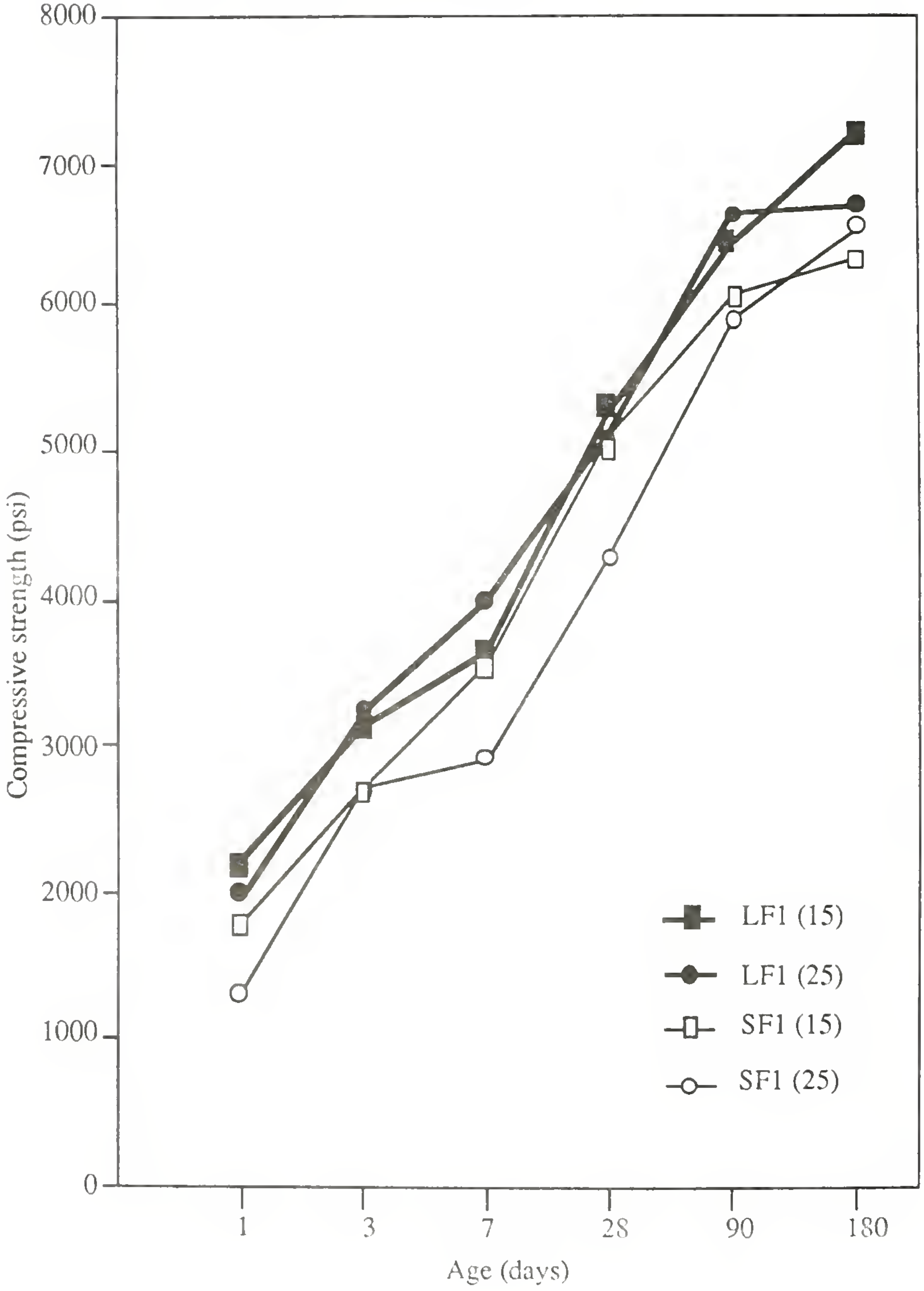

Figure 9.3-10 The compressive strength-curing time relationship for a fly ash concretes (fly ash F1).

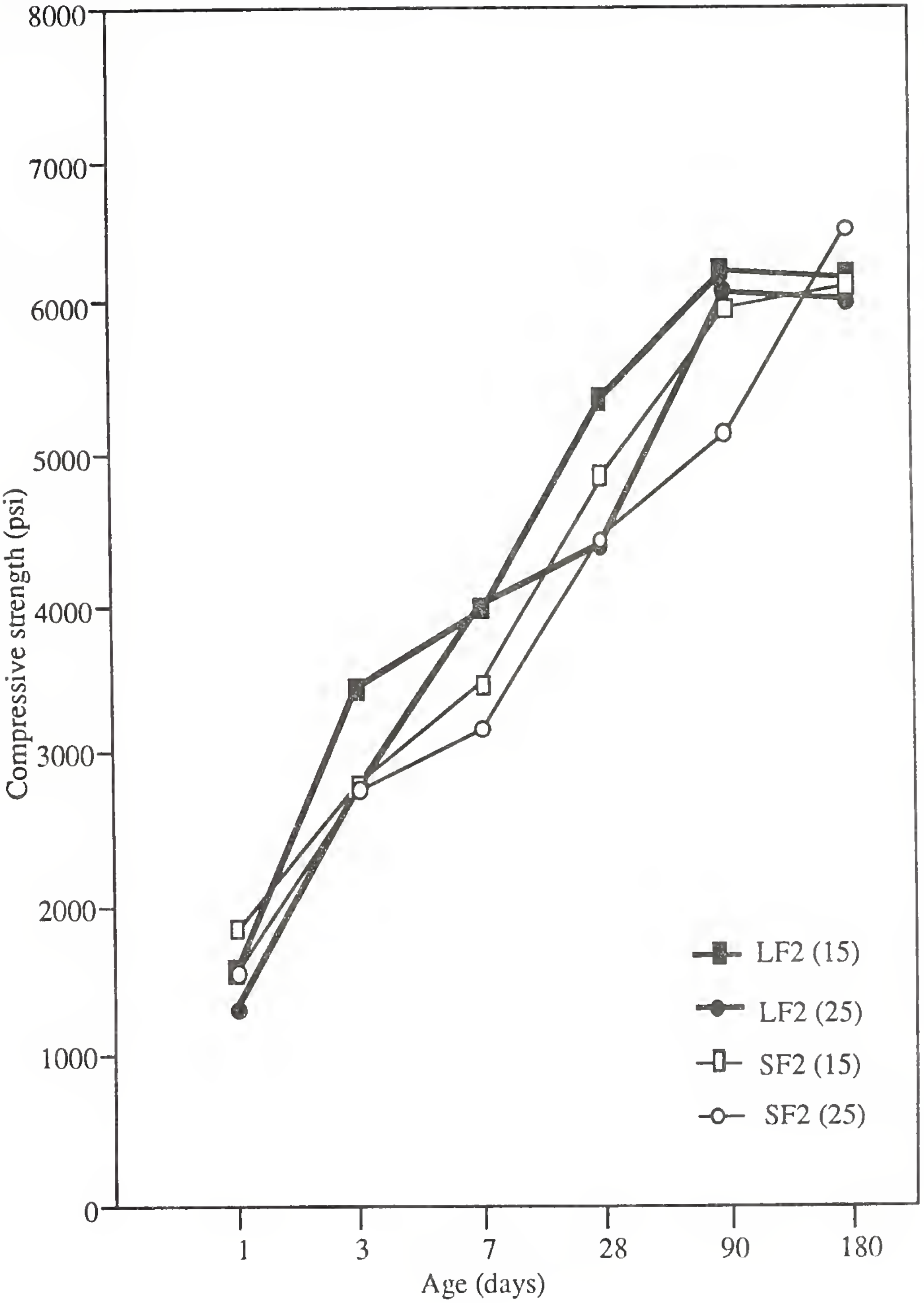

Figure 9.3-11 The compressive strength-curing time relationship for a fly ash concretes (fly ash F2).

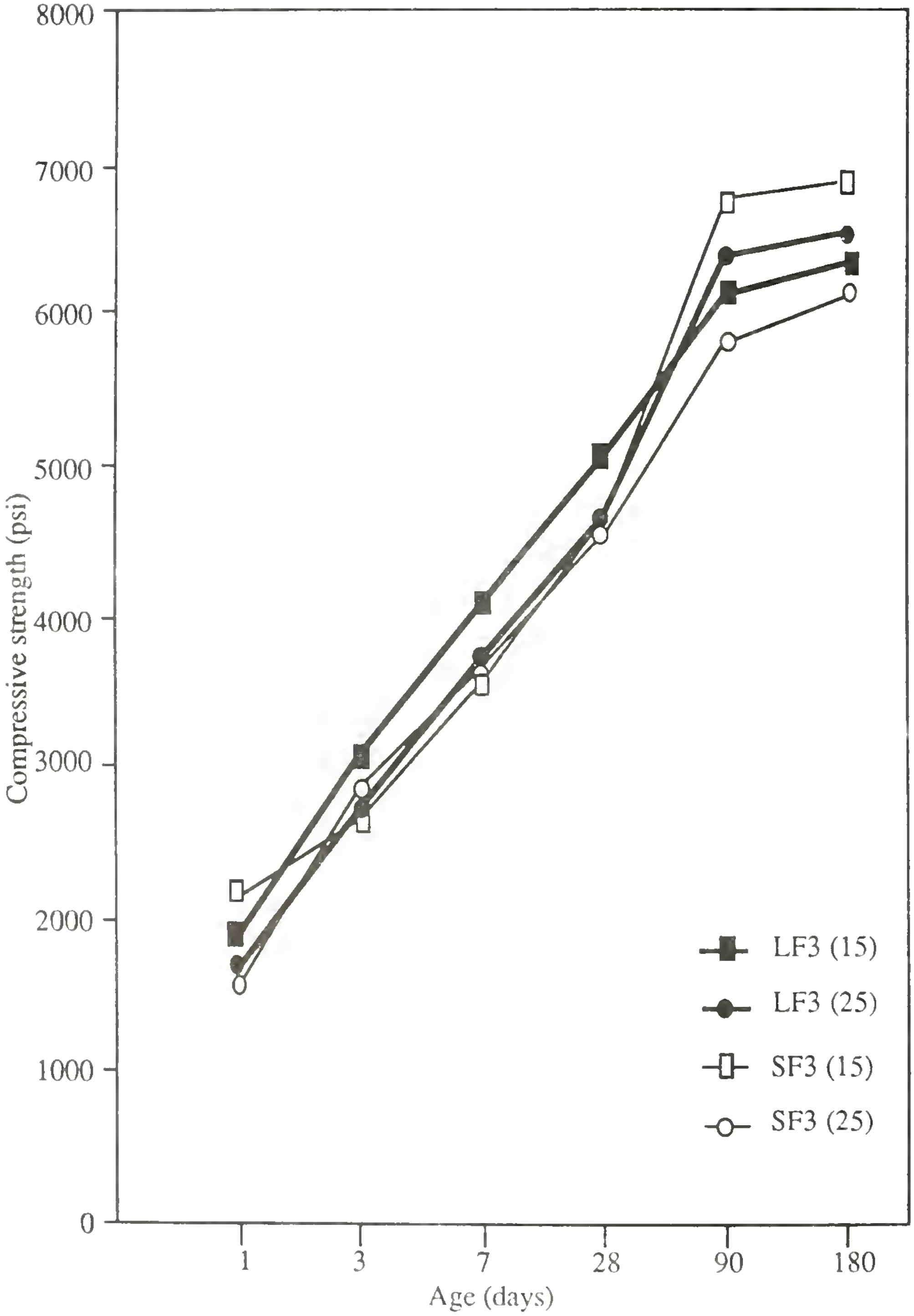

Figure 9.3-12 The compressive strength-curing time relationship for a fly ash concretes (fly ash F3).

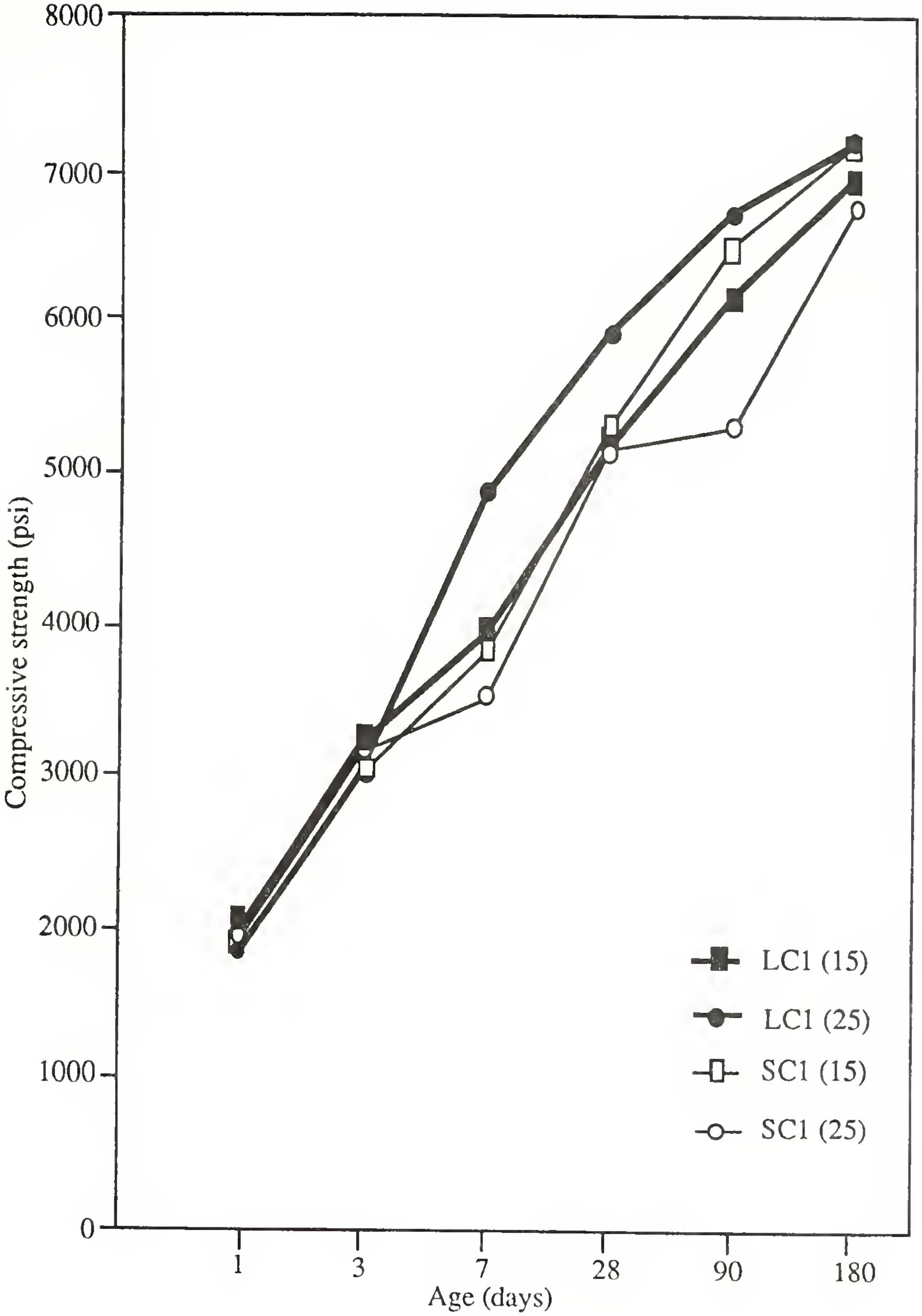

Figure 9.3-13 The compressive strength-curing time relationship for a fly ash concretes (fly ash C1).

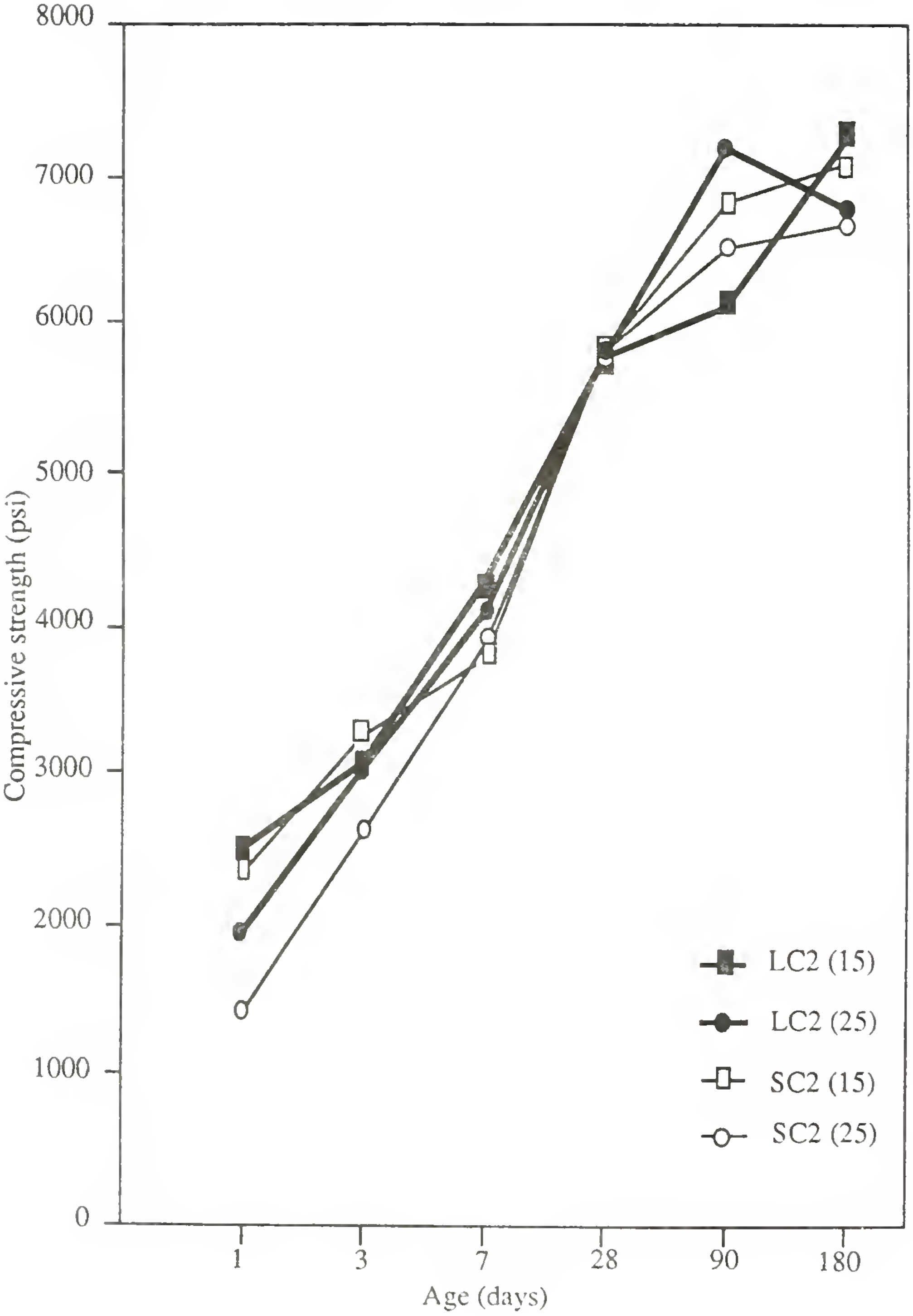

Figure 9.3-14 The compressive strength-curing time relationship for a fly ash concretes (fly ash C2).

25% replacement level. However, as the curing period is extended, the latter approach and frequently exceed the former, as can be seen for example in Figures 9.3-10, 9.3-12, 9.3-13 and 9.3-14.

Concretes made with cement S do not show this trend, and almost universally strengths at 25% replacement are slightly lower than at 15% replacement.

The preceding comparisons have been with respect to compressive strength. A corresponding series of flexural strength comparisons are given in Figures 9-3.15 to 9.3-20.

Fig. 9.3-15 compares the flexural strength development of plain reference concrete made with cements L and cement S. It is evident that although the flexural strengths of both series increase steadily with time, plain concrete made with cement L show a higher rate of flexural strength gain. The difference recorded reached a maximum of about 200 psi (27%) after 7 days of curing.

Between 7 and 28 days the flexural strength gain for the cement L - based concretes slows considerably; conversely, the rate of strength of cement S - based concrete increases.

For curing periods longer than 28 days, the flexural strength of cement L concrete stabilizes at the level of about 940 psi. The strength then drops slightly, and at 180 days reaches the value of about 900 psi. Meanwhile, the flexural strength of cement S concrete continues to increase, and at 180 days it reaches that of the cement L concrete, both being about 900 psi.

Analysis of Figures 9.3-16 to 9.3-20 shows that for fly ash concretes, the flexural strengths obtained with one cement is similar

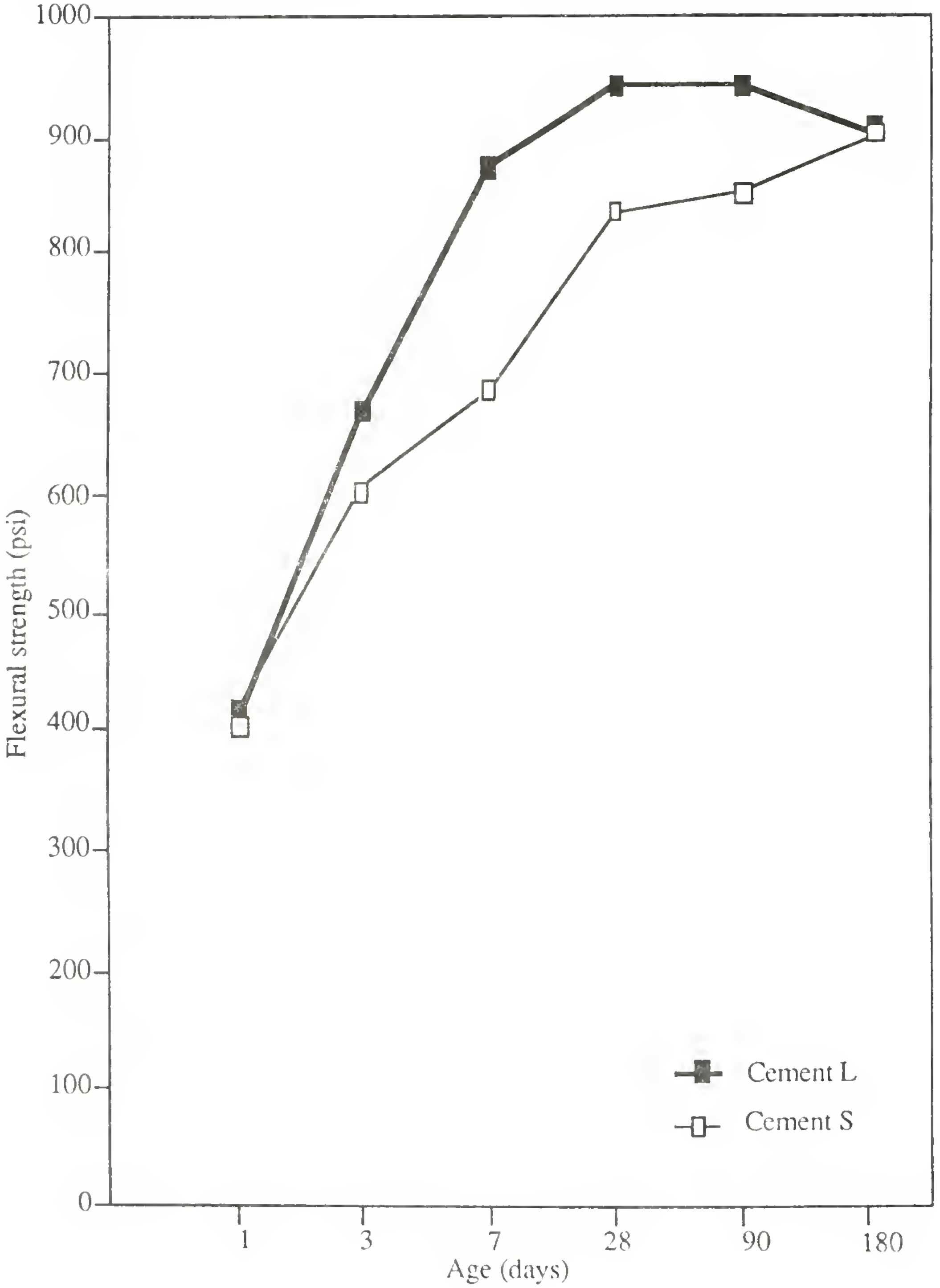

Figure 9.3-15 The flexural strength-curing time relationship for a plain concrete.

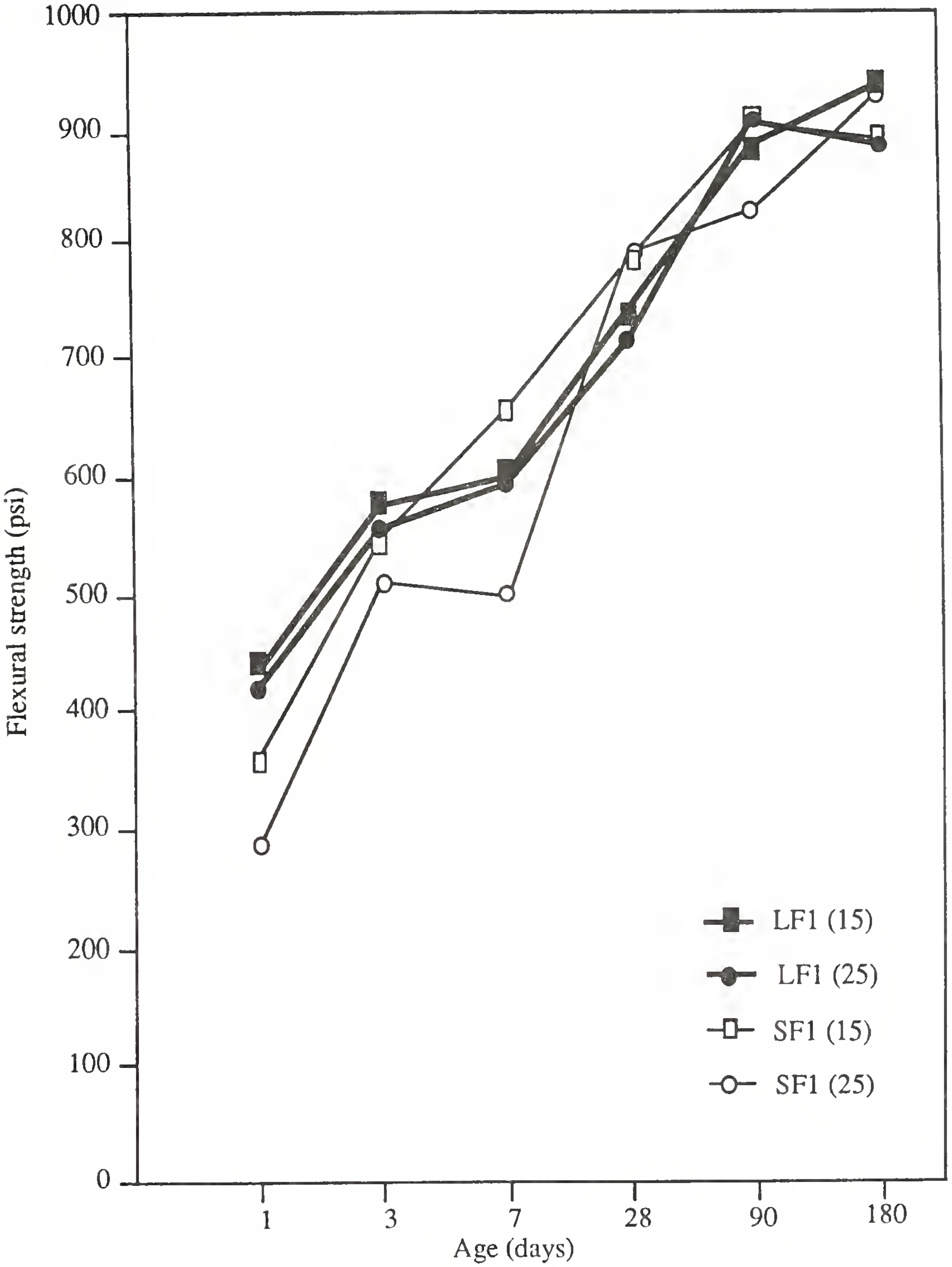

Figure 9.3-16 The flexural strength-curing time relationship for a fly ash concretes (fly ash F1).

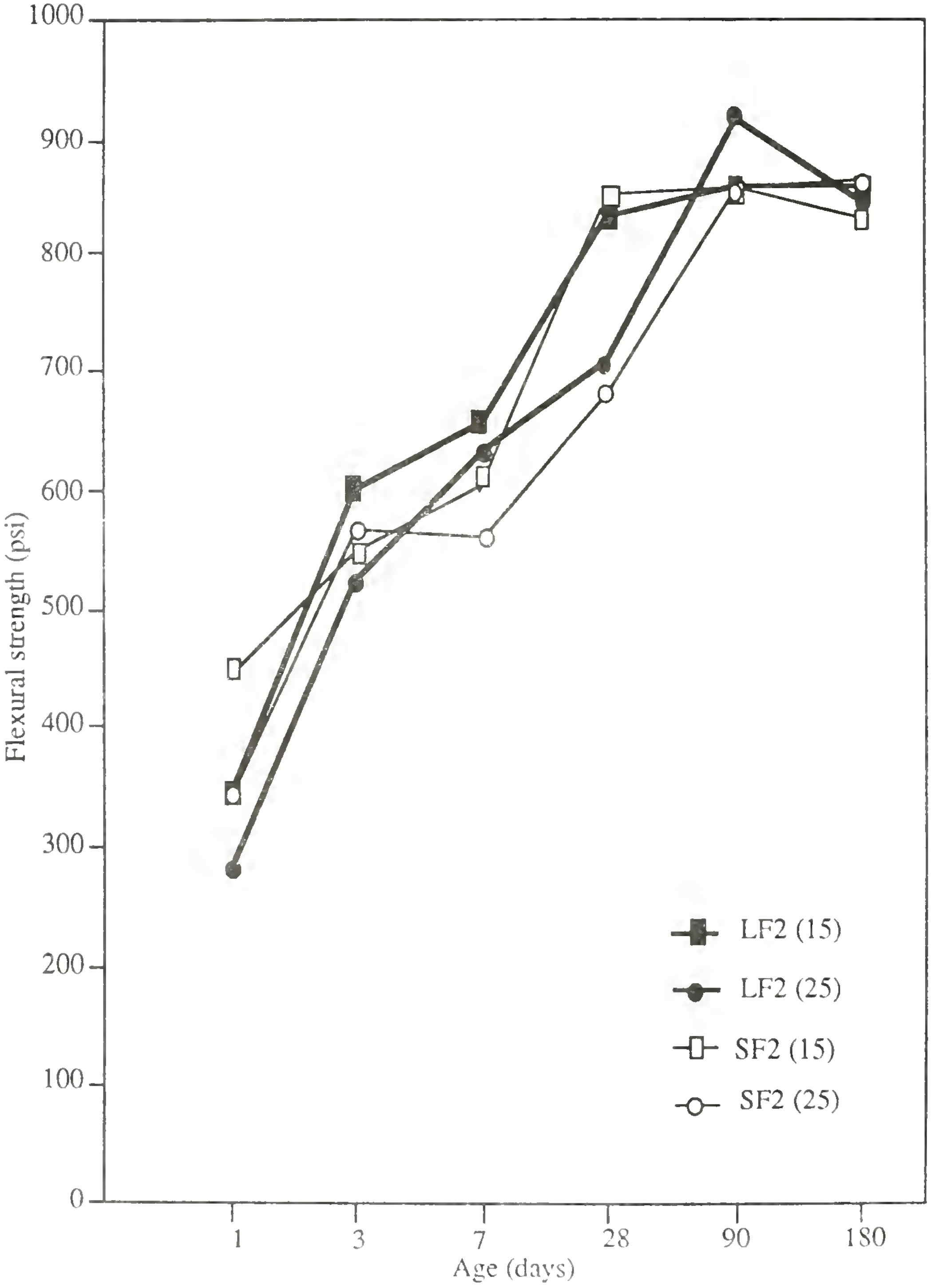

Figure 9.3-17 The flexural strength-curing time relationship for a fly ash concretes (fly ash F2).

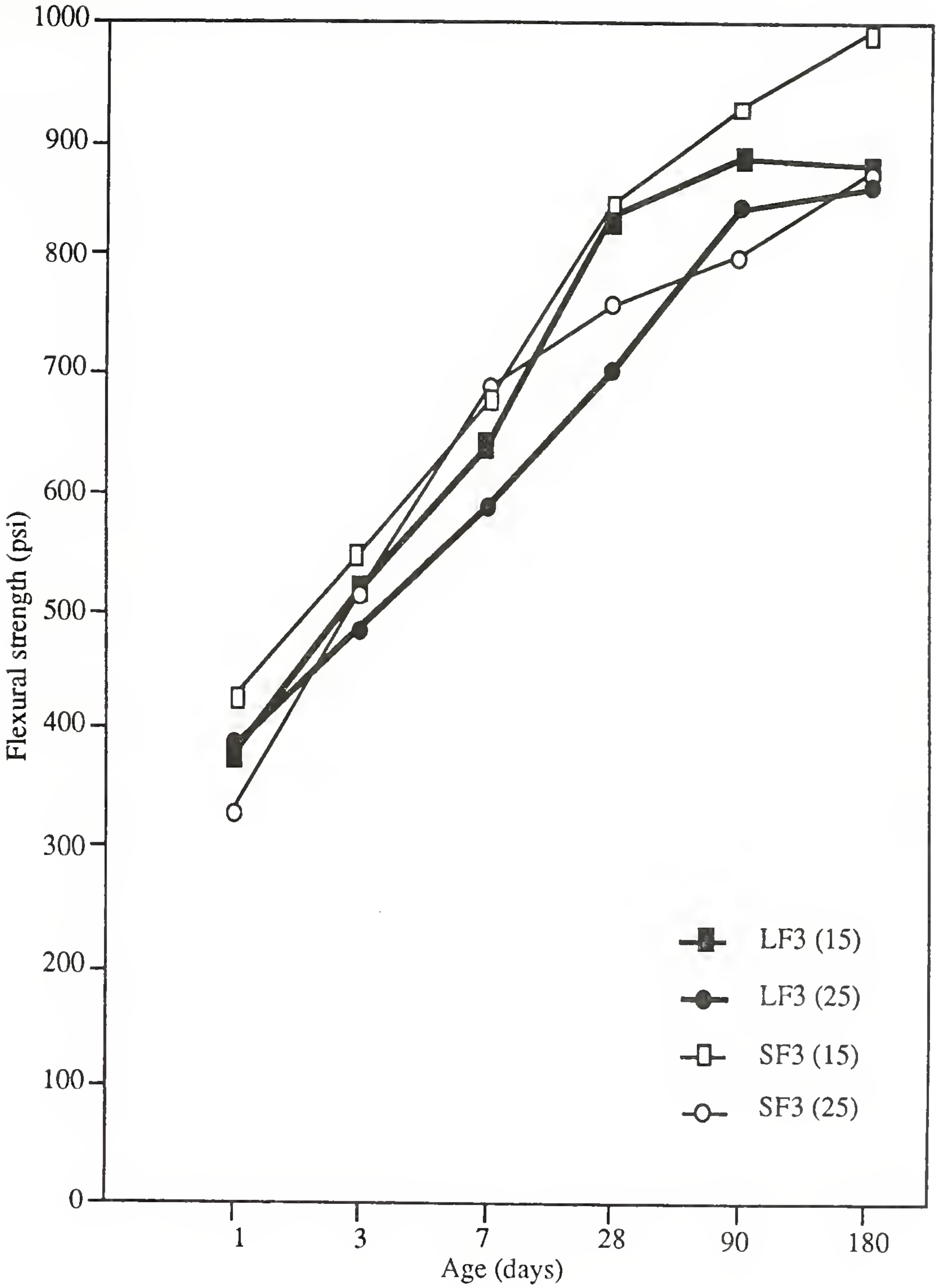

Figure 9.3-18 The flexural strength-curing time relationship for a fly ash concretes (fly ash F3).

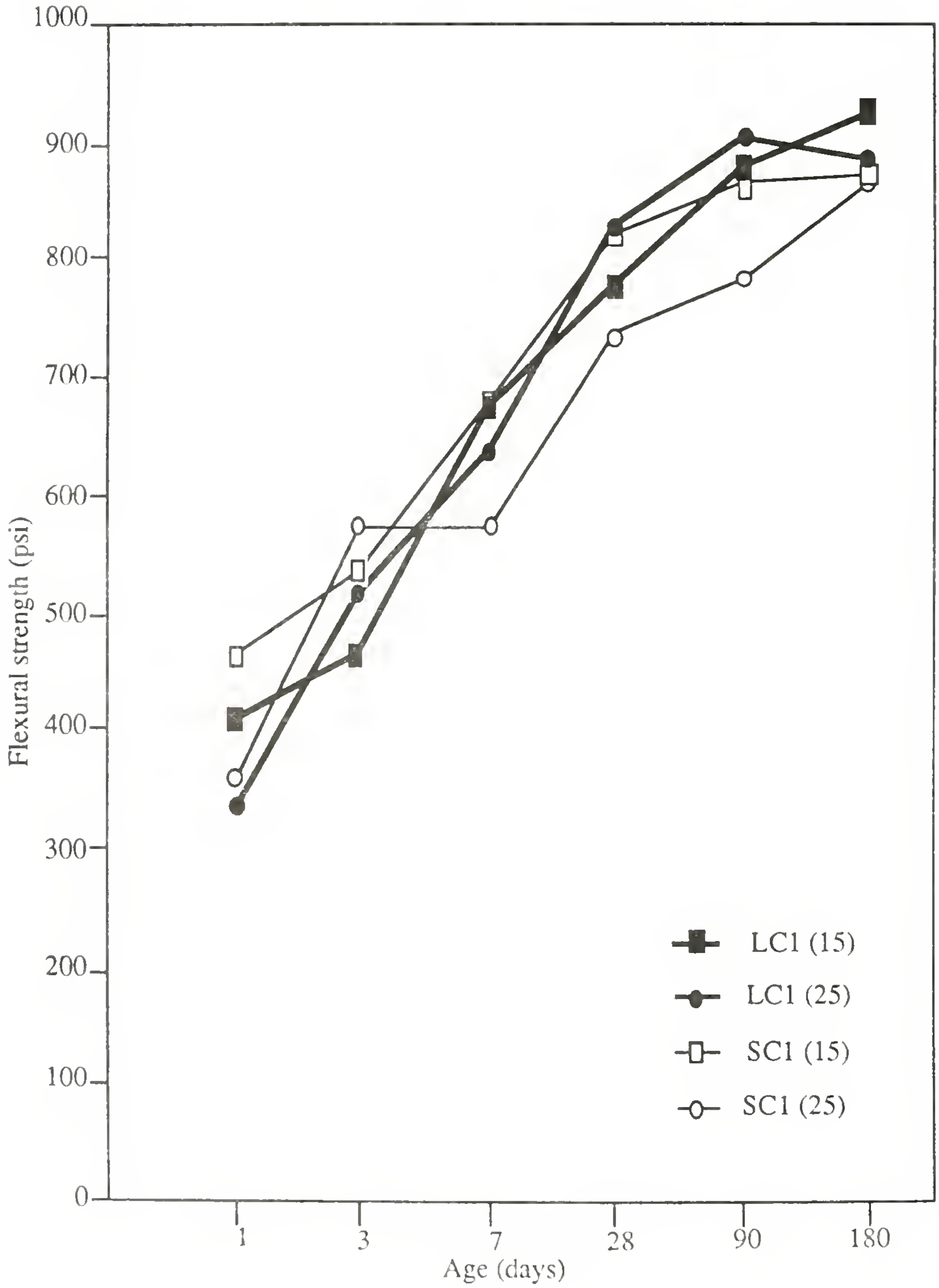

Figure 9.3-19 The flexural strength-curing time relationship for a fly ash concretes (fly ash C1).

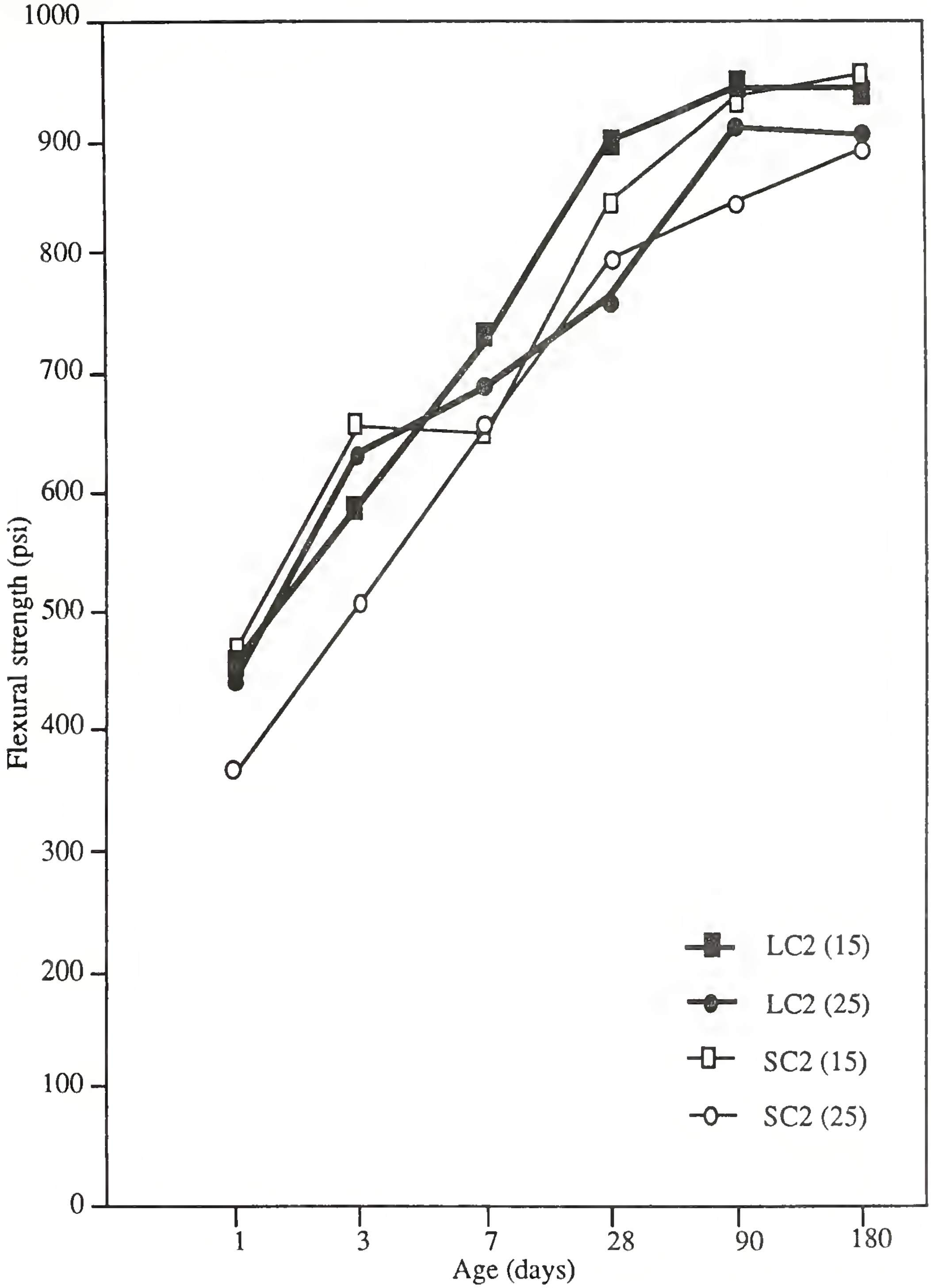

Figure 9.3-20 The flexural strength-curing time relationship for a fly ash concretes (fly ash C2).

to that obtained with the other. Once fly ash is included, the differences between the cements with respect to flexural strength development seem to disappear. For some combinations the cement L-based concretes were stronger in flexure (for example, see the 3 and 7 day values in Figures 9.3-16); for others the cement S-based concretes were stronger (see for example Fig. 9.3-19 for 1 day and 7 day comparisons.)

It also appears that, with flexural strength, unlike compressive strength, 25% replacement almost always results in a lower strength than does 15% replacement, regardless of the cement used. The differences are not very significant, however, and usually do not exceed 10%.

9.4 Density of Hardened Concretes

The densities of the hardened concretes at each age were determined so as to provide for possible correlation of density with concrete strength development.

The density measurements were performed following the procedure described in Section 4.9.3. All of the 22 varieties of concretes used in the course of this research program were measured, and measurements of density were taken after 1, 3, 7, 28, 90 and 180 days of curing. The results are presented in table 9.4-1. Each number in this table represents the average of two replicate density determinations.

The results presented in Table 9.4-1 clearly show that, with a few exceptions, the densities of all concretes increased with time. Comparison of the 1-day and the 180-day density values indicates that

Table 9.4-1. Summary of densities of hardened concretes as a function of their composition and curing time.

Mix	Curing Time (days)					
	1	3	7	28	90	180
	Density (g/cm^3)					
L	2.341	2.355	2.409	2.438	2.503	2.518
LF1(15)	2.464	2.429	2.432	2.461	2.530	2.589
LF2(15)	2.383	2.426	2.529	2.488	2.549	2.561
LF3(15)	2.324	2.341	2.499	2.476	2.550	2.581
LC1(15)	2.346	2.418	2.492	2.461	2.539	2.577
LC2(15)	2.383	2.374	2.439	2.522	2.576	2.636
LF1(25)	2.350	2.455	2.473	2.480	2.487	2.557
LF2(25)	2.357	2.367	2.454	2.453	2.522	2.506
LF3(25)	2.354	2.345	2.462	2.453	2.491	2.542
LC1(25)	2.431	2.426	2.409	2.484	2.545	2.569
LC2(25)	2.357	2.382	2.424	2.480	2.540	2.579
S	2.335	2.359	2.364	2.419	2.533	2.581
SF1(15)	2.332	2.363	2.435	2.522	2.561	2.610
SF2(15)	2.376	2.411	2.432	2.507	2.514	2.516
SF3(15)	2.387	2.374	2.454	2.480	2.580	2.613
SC1(15)	2.401	2.370	2.413	2.461	2.506	2.573
SC2(15)	2.409	2.374	2.465	2.529	2.564	2.597
SF1(25)	2.332	2.378	2.323	2.408	2.472	2.553
SF2(25)	2.372	2.385	2.405	2.495	2.499	2.534
SF3(25)	2.394	2.392	2.458	2.476	2.495	2.483
SC1(25)	2.369	2.407	2.391	2.507	2.425	2.530
SC2(25)	2.382	2.392	2.428	2.508	2.490	2.550

the overall relative increase was about 8%. This number seems to be independent of the replacement level and the kind of cement or fly ash used in a given concrete.

Examination of the data in Table 9.4-1 reveals that, irrespective of the specific cement or fly ash used and of their proportions in the mix, at any given age the density values of all of the concretes examined are very close to each other. In other words the actual variation in density among the concretes of a given age are so insignificant that it would be difficult to correlate them with the significant differences in strength development observed for the same mixes.

These findings indicate that neither the actual density values nor their changes with time are sensitive enough to reflect variations in the internal structure of concretes resulting from the incorporation of the different fly ashes. The density data similarly do not permit quantitative assessment of differences in the progress of the pozzolanic reaction with time.

It should be stressed however, that the continuous increase in all of the density values indicates the progressive densification of the internal structure of all the concretes. The measurement may be useful also in that unexpected changes in density, especially reductions, may serve as indicators that processes of internal deterioration are occurring that may influence the performance of a given concrete.

10.0 EFFECTS OF FLY ASH ON DURABILITY RELATED PROPERTIES

One of the major concerns in introducing the use of fly ash for highway concrete is to be able to provide assurance that the durability characteristics of the concrete being produced will not suffer from inclusion of the fly ash.

Indeed, this concern was one of the primary reasons this project was undertaken, and one of the serious questions that need to be answered before large scale use of fly ash for highway concrete can be recommended. Highway concrete, particularly pavement concrete, is subjected to a far more difficult service environment than most concretes destined for use either in building construction or in mass concreting.

The primary reason for the development of the CPQ mix design procedure was to insure that, to the extent possible, adjustments in mix water in response to variations in fly ash properties do not degrade the durability of the material being produced.

In this section we present the results of a number of tests and investigations on durability-related properties of the concretes under study. Some of these were measured, by necessity, not on the concrete per se but on cement paste batched from the same constituents and proportions as used in the concrete, but without aggregate.

10.1 Mercury Porosimetry

Measurements of porosity and pore size distribution using mercury porosimetry are often cited as a prime index of the potential resistance of a given concrete to durability problems. Many durability problems affecting concrete involve diffusion or mass transfer of deleterious chemical components from outside the concrete. Also, resistance to freezing and thawing is in part related to the pore characteristics of the concrete, although freezing problems may generally be prevented by the inclusion of an adequate air bubble system.

Generally speaking, the smaller the extent of paste porosity and the finer the pore size distribution, the more resistant the given concrete will tend to be to most durability problems.

In this study mercury porosimetry testing was carried out on pastes prepared at the 25% replacement level as defined earlier, at a w:/(c+fa) ratio of 0.49, thus duplicating the paste composition in the concretes. All specimens were sealed and hydrated for approximately 1 year (actual age varied between 363 and 377 days) before sampling. Thus the pore size distributions obtained are those of nature pastes, and are not likely to change with further ageing.

Each paste was run at least in duplicate, with the results presented being the average distributions for all of the runs made for a given paste. All specimens were oven dried prior to mercury porosimetry, and a contact angle of 116°, appropriate to this condition, was used.

Figure 10.1-1 provides results for the cement paste and all of the

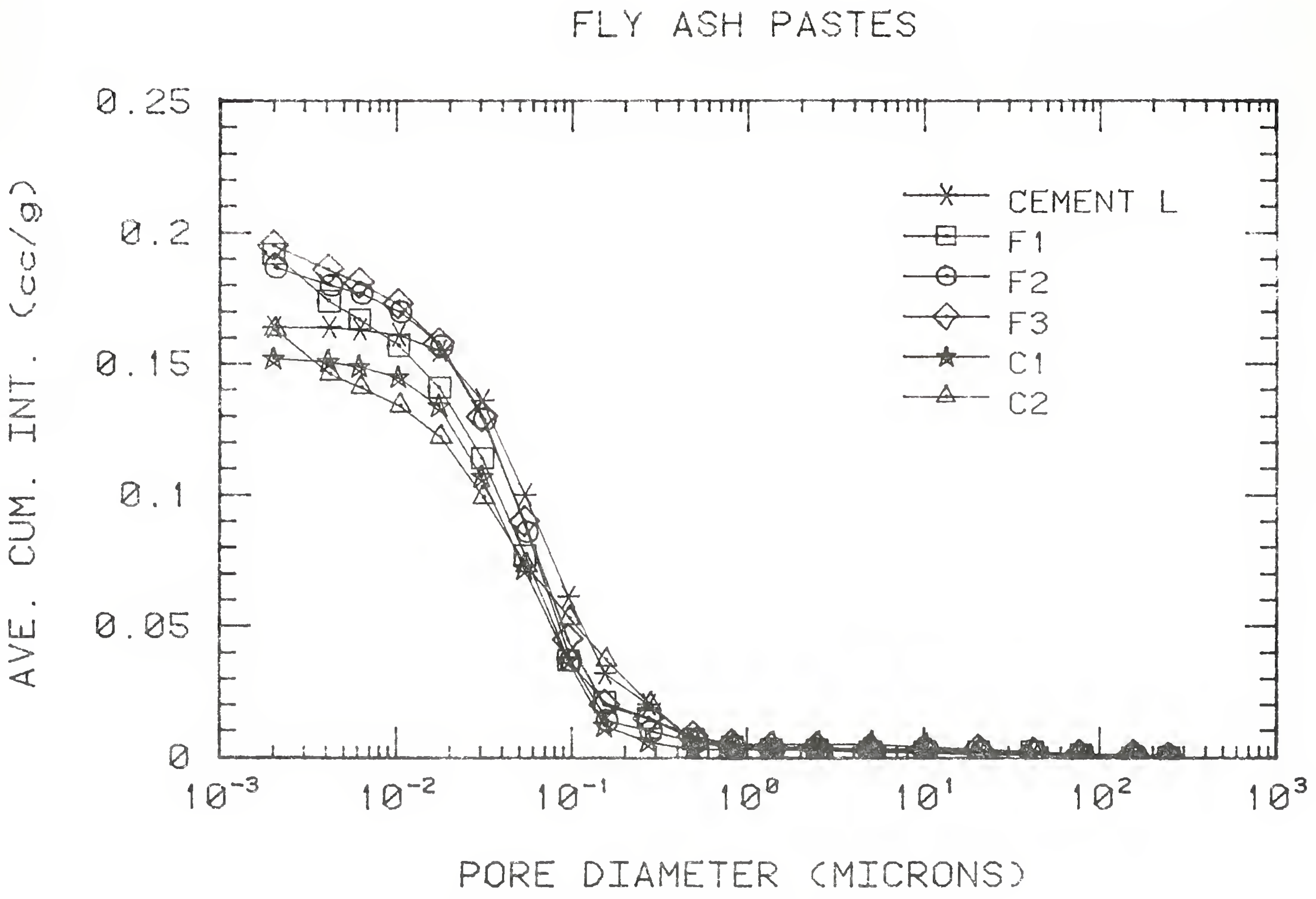

Figure 10.1-1 Mercury intrusion pore size distribution curves for all pastes.

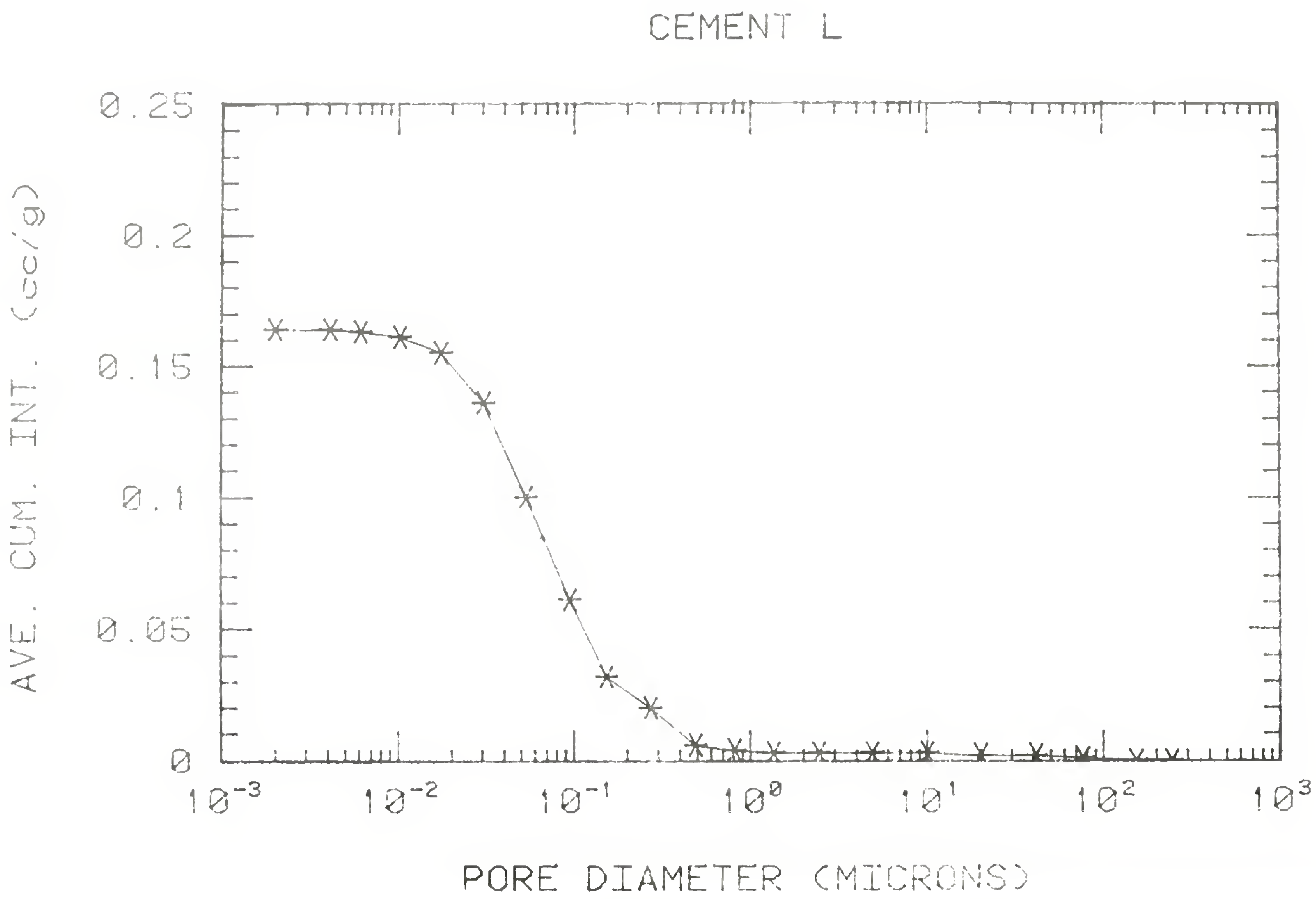

Figure 10.1-2 Mercury intrusion pore size distribution curves for cement paste L.

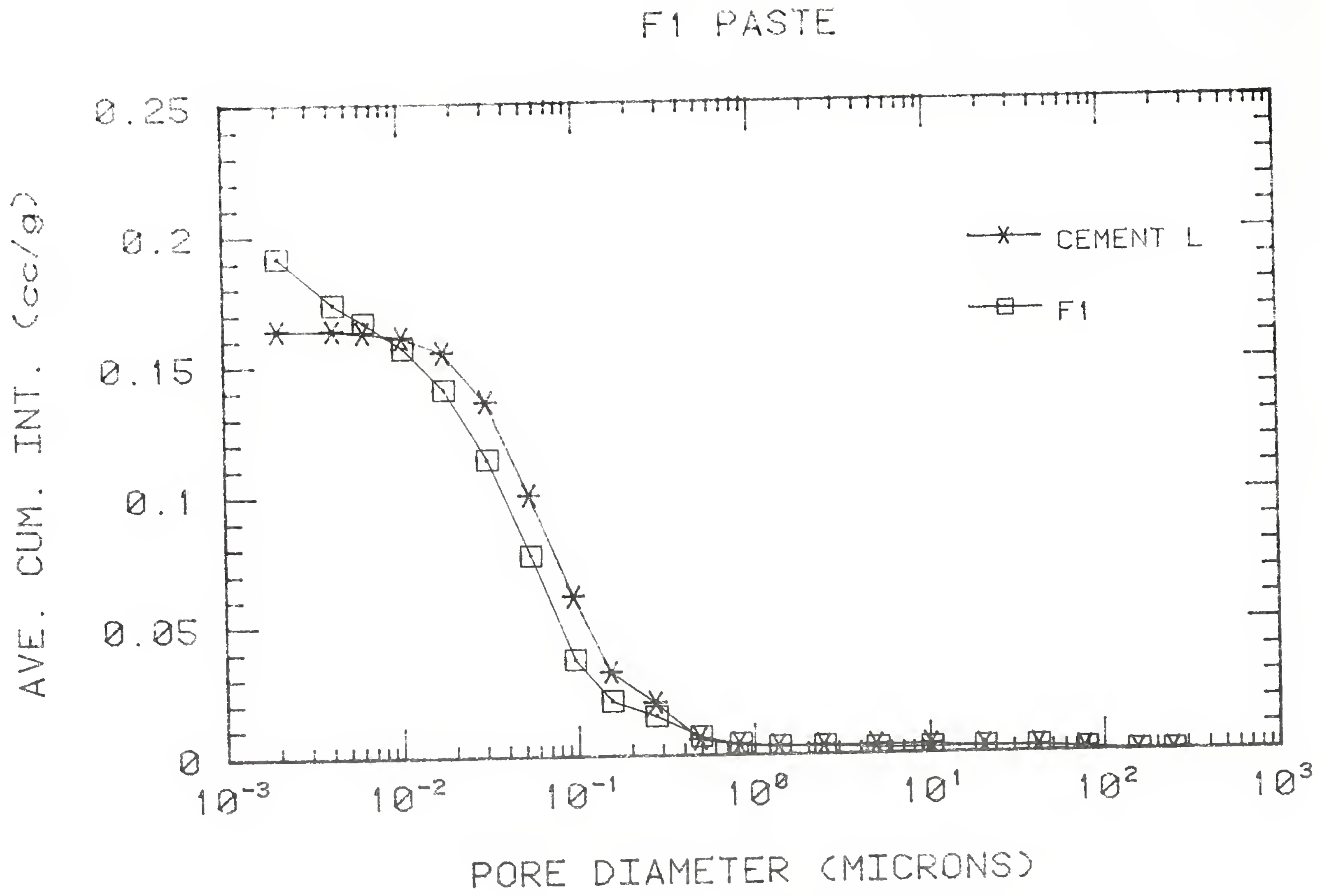

Figure 10.1-3 Comparison of mercury intrusion pore size distribution curves for cement paste L and fly ash paste with F1 ash.

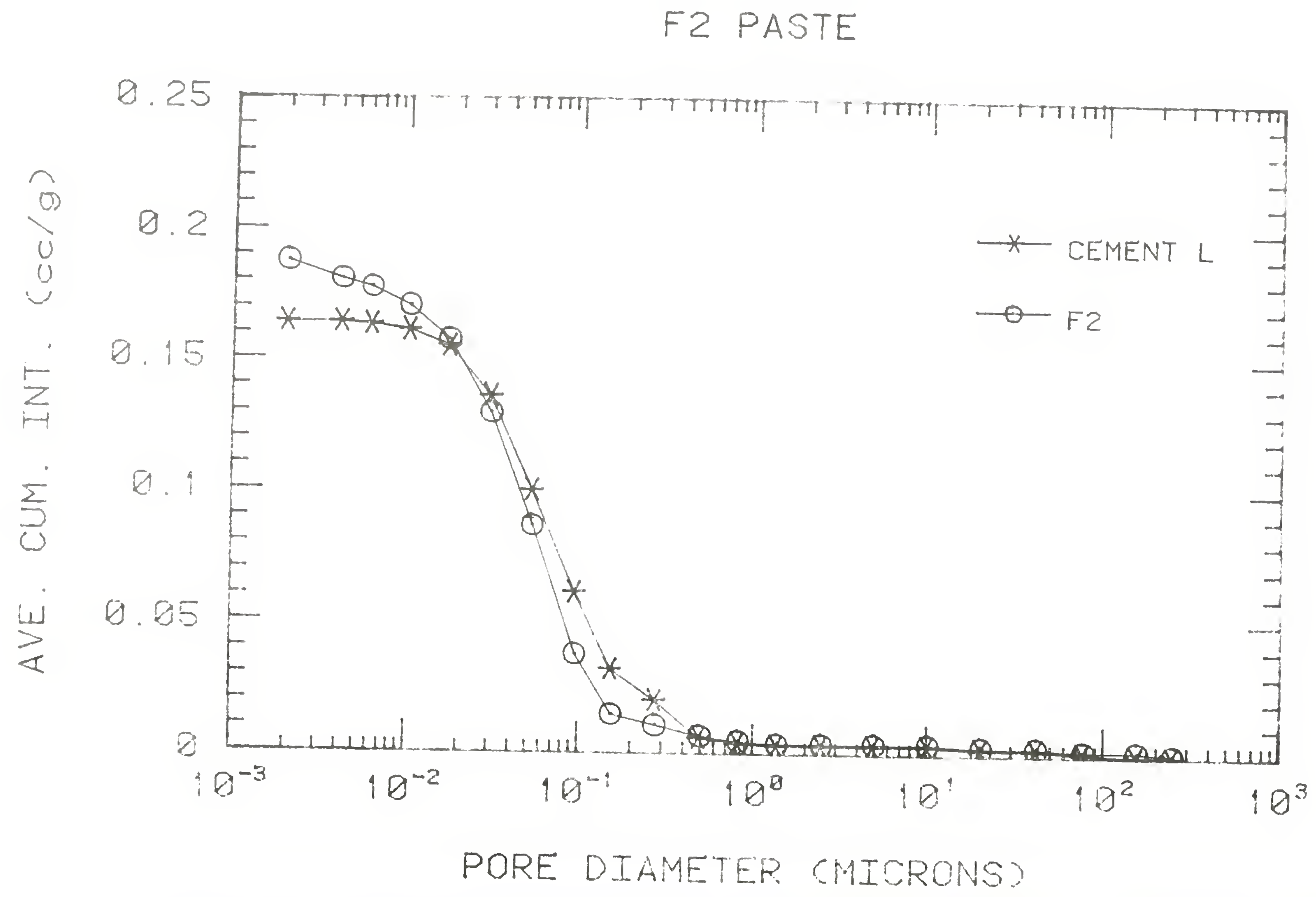

Figure 10.1-4 Comparison of mercury intrusion pore size distribution curves for cement paste L and fly ash paste with F2 ash

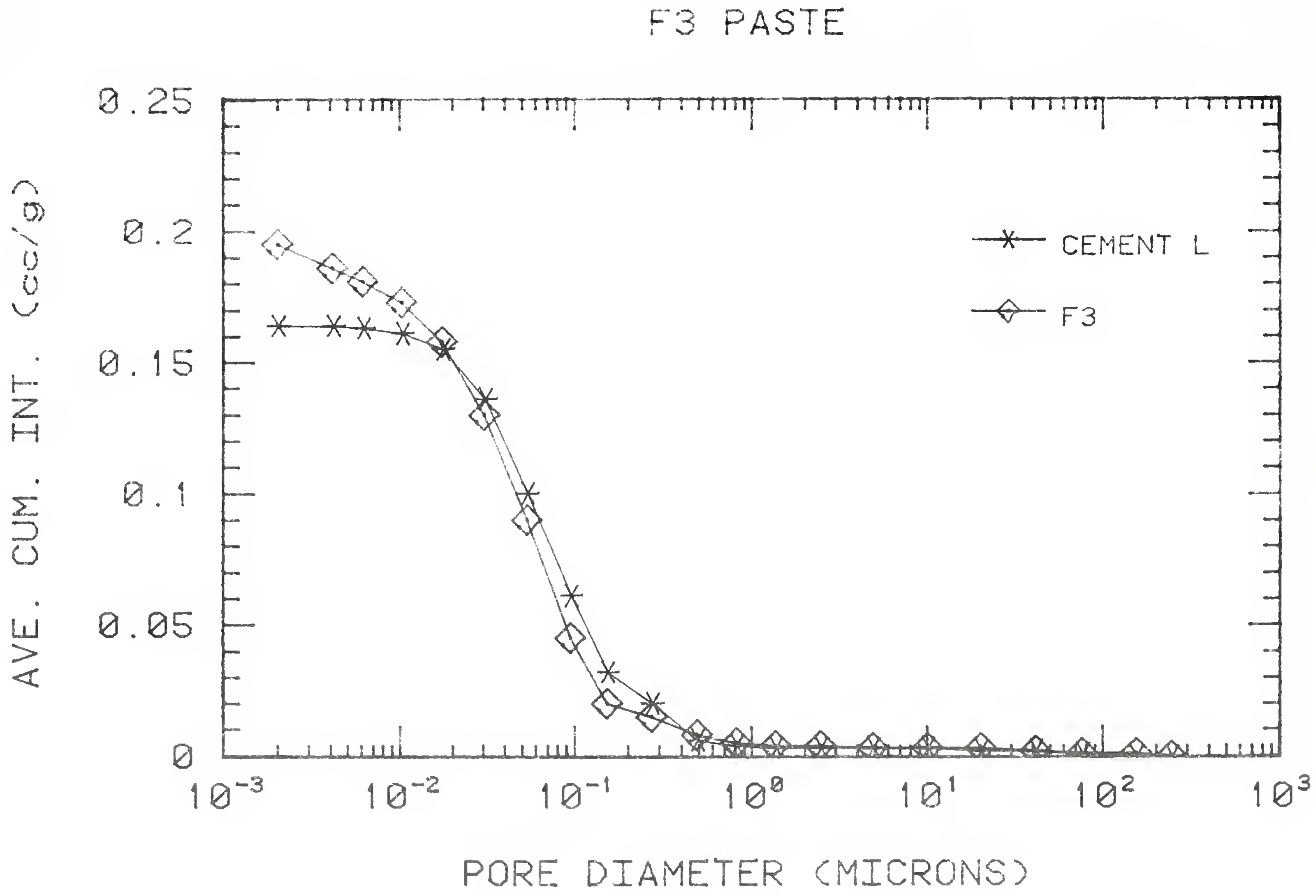

Figure 10.1-5 Comparison of mercury intrusion pore size distribution curves for cement paste L and fly ash paste with F3 ash.

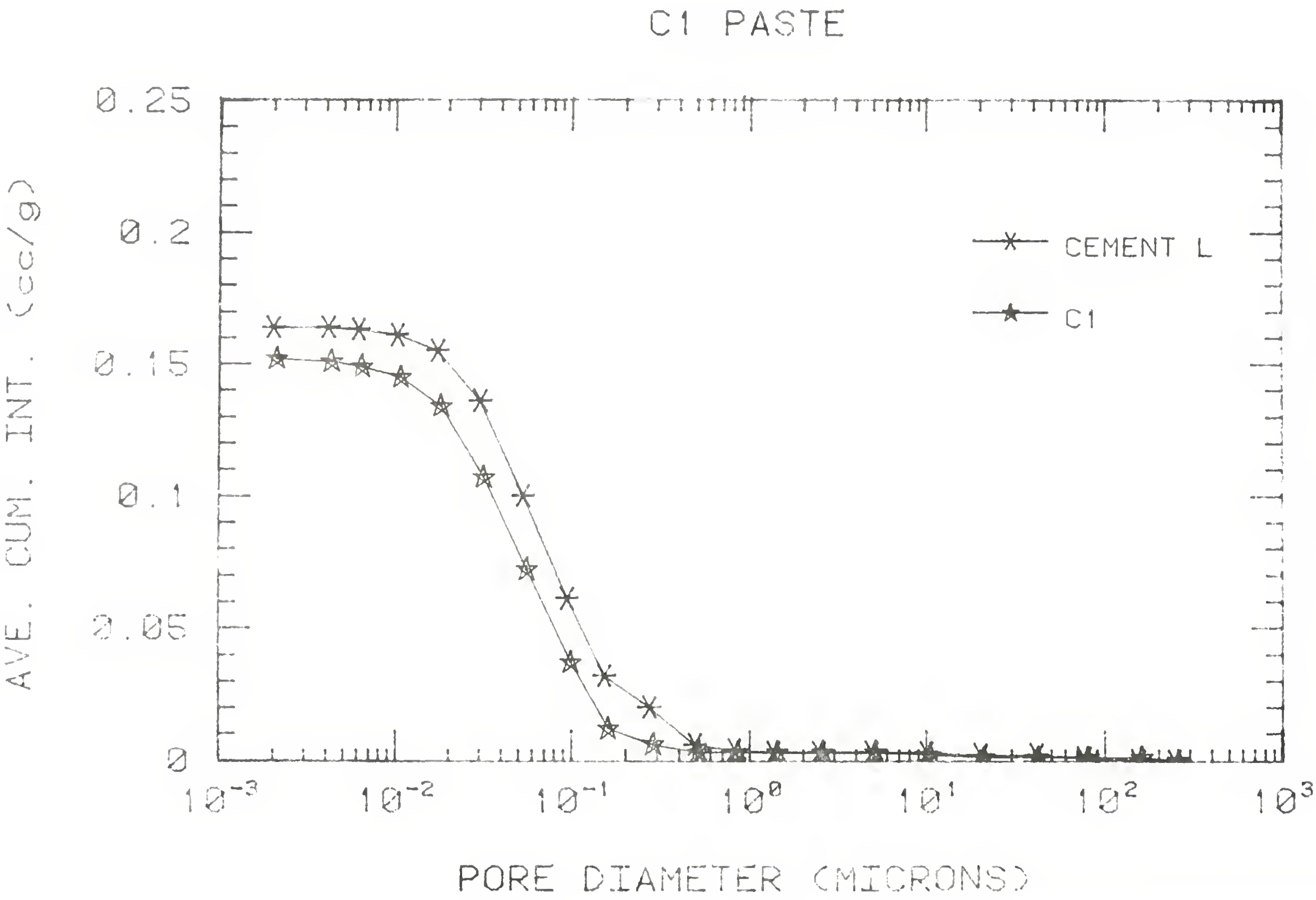

Figure 10.1-6 Comparison of mercury intrusion pore size distribution curves for cement paste L and fly ash paste with C1 ash.

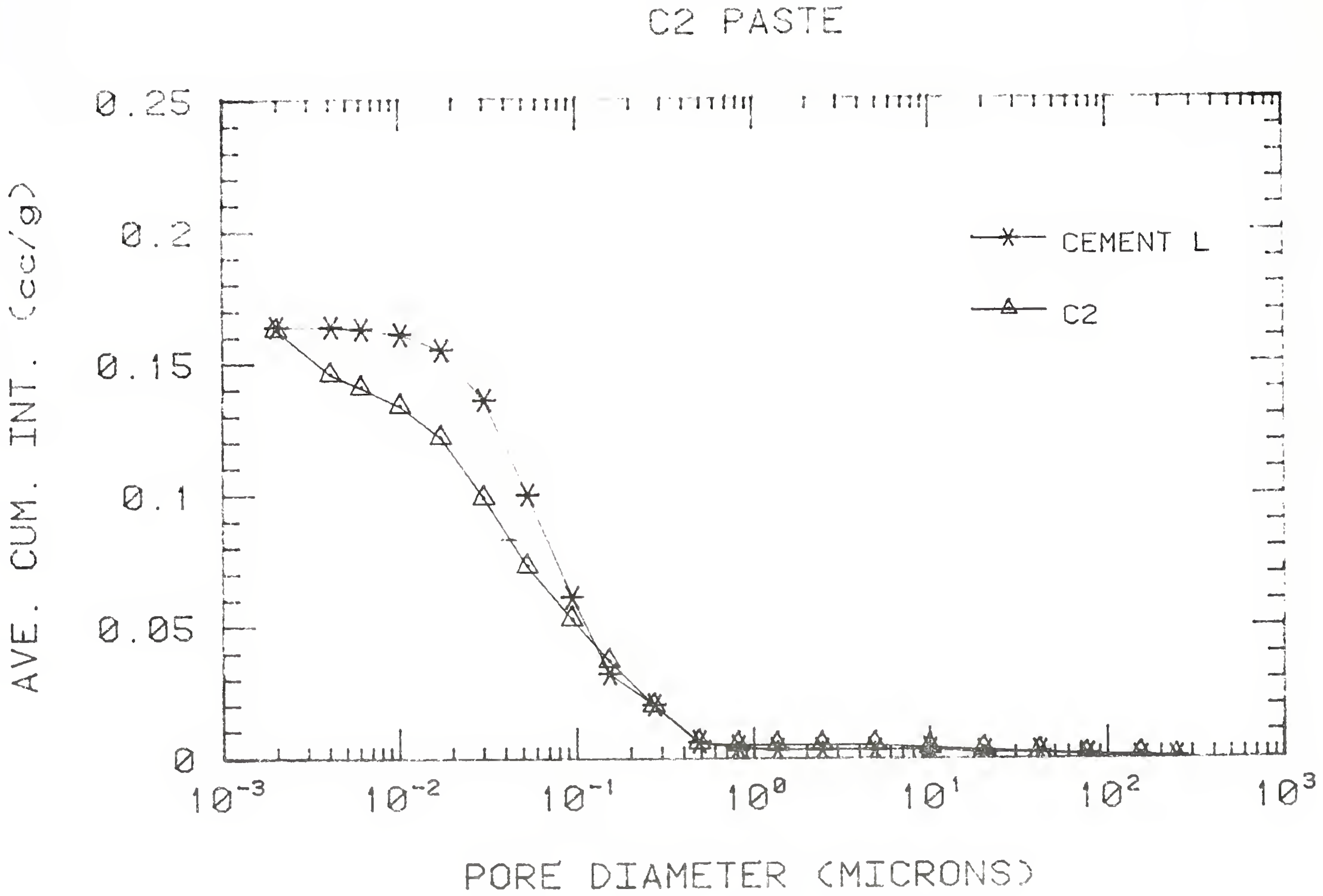

Figure 10.1-7 Comparison of mercury intrusion pore size distribution curves for cement paste L and fly ash paste with C2 ash.

fly ash-bearing pastes, shown together to permit general examination. Figures 10.1-2 shows the pore size distribution of the reference cement paste by itself; Figures 10.1-3 to 10.1-7 show individual comparisons between the reference cement paste and each fly ash-bearing paste.

Examination of Figure 10.1-1 indicates that the pastes have generally similar particle size distributions. The total pore volumes intruded at pressures up to the maximum 60,000 psi range between 0.15 and 0.20 cc/g of paste, and none of the pastes show any significant pore volume in pores coarser than about 0.5 µm. However, there are individual differences whose significance need to be examined.

Figure 10.1-2 by itself reveals the following features:

(1) The "break-through" diameter, i.e. the diameter at which major intrusion starts, is at 0.50 µm (5,000 A).

(2) The total intruded pore volume is about 16.5 cc/g.

(3) The mean diameter of the indicated pore system is about 0.065 µm (650 A).

(4) There is very little indicated pore volume below 0.01 µm (100 A).

These are reasonably typical characteristics for pore size distributions of mature cement pastes of this range of w:c ratio. Figure 10.1-3 provides a comparison of the pore size distribution curves for the F1 fly ash paste and the reference cement paste. Some differences are apparent, including:

(1) The F1 paste has a higher total intruded volume, about 0.19 cc/g.

(2) This extra porosity occurs in the finest pore size range, well

below about 0.008 µm (80 A).

(3) The mean pore diameter is about 0.04 µm (400 A), significantly finer than the mean pore diameter of the reference cement paste, and the bulk of the curve is displaced to the left of it, i.e. to the finer sizes.

These differences suggest that incorporation of the F1 ash has produced a finer, that is a "tighter" pore system, i.e. one that would be associated with improved durability characteristics. The extra pore volume in the finest pores is indicative of the formation of extra cement gel by an effective long term pozzolanic reaction of this fly ash.

Figure 10.1-4 shows that the paste incorporating fly ash F2 has developed a pore system whose characteristics are very similar to those described for the F1 paste above. All of the comparisons made previously between the F1 paste and the reference cement paste hold good in a qualitative sense here as well. Quantitatively the numbers are almost the same; the total intruded volume is just under 0.19 cc/g, the mean pore diameter is slightly higher (about 0.05 µm or 500 A), and the "extra" pore volume extends to slightly coarser pore sizes, to about 0.015 µm (150 A) instead of only to 8.008 µm (80 A). This paste is also one that we judge should have better durability characteristics than the reference cement paste, although perhaps not quite as good characteristics as that generated with the F1 fly ash.

Figure 10.1-5 shows the same comparison for the last of the Class F fly ashes, F3. The pore size distribution curve for the F3 paste is almost identical to that for the F2 paste, and the same conclusions apply.

The curves for the pastes batched with the Class C fly ashes are both different in character from those batched with the Class F fly ashes described above, are also different from each other.

Figure 10.1-6 shows the comparison between the curves for the C1 paste and the reference cement paste. Here a rather different set of features are noted:

(1) The "break-through diameter" is finer for the fly ash paste, about 0.02 μm (200 A) instead of the approximately 0.05 μm (500 A) previously observed.

(2) The total intruded volume for the C1 paste is less, not greater than that of the reference paste, i.e. there is no extra pore space in the finest sizes, and

(3) There is no crossing over of the curves; the fly ash paste shows a smaller volume of intruded pores at all sizes.

The mean pore diameter here turns out to be about 0.05μm (500 A), essentially identical to those for the F2 and F3 pastes, but the other characteristics of the particle size distribution curve are different. They are also different from those of the other paste with Class C fly ash, C1, the curve for which is shown in Figure 10.1-7. The comparison here shows:

(1) The break-through diameter is the same as for the reference cement and Class F fly ash pastes.

(2) The total intruded volume is the same as that for the reference cement paste, but

(3) The shape of the size distribution curve is different from that

of the reference cement paste or the C1 paste, and resembles those for the Class F fly ashes. The pore structure is thus also finer than that of the reference paste, but finer in a different way than the C1 paste.

The mean particle diameter here turns out to be about 0.04 μm (400 A), finer than that for the C1 paste and similar to that of the F1 paste.

Thus both Class C fly ash pastes show finer pore size distributions than the reference cement paste, and to that extent, should indicated better durability characteristics. Whether the kind of distribution shown for C1 is "better" or "worse" than the kind of distribution shown for C2 is not possible to say with certainty at this stage.

It should also be noted that the cement paste in actual concrete does not necessarily have the same pore size distribution as the "same" paste batched separately. The presence of the sand grains in concrete modifies the pore structure somewhat. Determining valid pore size distributions for the paste actually in concrete is, for technical reasons, a major research undertaking in itself, and would almost require a separate project to be successful. We believe that the differences between the different separately batched pastes examined here would also be present if the actual concrete pastes could be examined, but that all of the size distributions would be modified.

10.2 Chloride Permeability of Fly Ash Concrete

One of the most frequently used new tests for durability characteristics of concrete is the so-called "chloride permeability" test, developed originally by Whiting [218]. The actual measurement is of total charge, in coulombs, passed through a 2-inch thick disc sample of the concrete under the influence of a continuous DC potential over a period of six hours. The charge is carried primarily by chloride ions migrating into the concrete from a sodium chloride reservoir in contact with one of the faces of the specimen.

This test was developed as a rough indicator of the effective resistance of saturated concrete to migration of chloride ions, although it actually measures the electrical conductance associated with this process over time. It is generally considered to be an indicator of relative water permeability as well as being more specifically an indicator of ease of chloride ion transmission. Generally speaking, the lower the indicated "permeability" (in coulombs), the tighter the concrete pore structure is assumed to be, and the more resistant it is expected to be to various durability problems.

Different concretes are known to vary significantly in their responses to this test procedure. In the interpretation provided in the AASHTO test method, a total charge transfer of > 4000 coulombs indicates "high" permeability, 2000 to 4000 coulombs "moderate" permeability, 1000 to 2000 coulombs "low" permeability, and 100 - 1000 coulombs "very low" permeability.

The results of the present tests, carried out for concretes moist cured for 6 months prior to testing are presented in Table 10.2-1 and in Figures 10.2-1 through 10.2-4. As previously described in Section 4.9.7, two specimen slices (one from the top and one from the bottom of the concrete cylinder) were tested for each concrete.

It has been previously established by the writers (and others) that high current flow in a more permeable concrete specimens leads to temperature rise, which appears to cause reductions in resistance over time, additional to any reductions over time caused by the chloride ion penetration into the concrete itself. Therefore, in the earlier measurements the temperatures of both the NaCl solution and the interior of the specimens were monitored using thermocouples. This practice was eventually discontinued, since for all of the specimens tested here the measured current values were very steady with time and for these concretes there was no observable increase in temperature.

The data indicate that all specimens originally sliced from the top of the concrete cylinders show greater permeability than the corresponding specimens sliced from the bottoms of the same cylinders. This is somewhat puzzling as no visible segregation or bleeding was observed for the fresh concretes. As the specimens sliced from the top of the cylinder were tested without any additional surface preparation, it is possible that the observed difference reflects disturbance to the internal structure of the top part of the concrete induced when finishing the upper surface of the fresh concrete. These relative differences tend to be higher for plain concrete mixes (L and S) and mixes containing the C1 and C2 high calcium fly ashes than for the mixes with the F1, F2, and F3 low calcium fly ashes.

It was found that incorporation of each of the fly ashes reduced the measured chloride permeability, i.e. all of the fly ashes were beneficial for every specimen tested. The degree of reduction of indicated permeability was found to be dependent on both the fly ash type and the replacement level. The low calcium fly ashes were more effective than the high calcium ones, and for either type of fly ash, higher replacement led to greater reduction in measured chloride permeability.

The actual chloride permeability values obtained are indicated in Table 10.2-1, and plotted schematically for comparison purposes in Figures 10.2-1 to 10.2-4.

Low calcium fly ash F1 was by far the most effective of the fly ashes used in the study. It was found that in concretes containing this particular fly ash the total charge passed (computed as the average of bottom and top values) was only 33% (at 15% replacement) or 22% (at 25% replacement) of the values of charge recorded for the plain concrete mixes. Of the two high calcium fly ashes, the C2 fly ash proved to be more effective than fly ash C1. At 25% replacement it reduced the total charge (on average) by a factor of 3.

A comparison of the measured chloride permeability data with the strength values for the same mixes indicates that higher strength does not necessarily mean less permeable concrete. In fact, the concretes containing high calcium fly ashes tend to be stronger in almost all cases despite the fact that their measured chloride permeability values also tend to be higher. This is an indication that factors other than

Table 10.2-1. Total charge (coulombs) passed during electro-osmosis.

Mix	Fly Ash Replacement (%)	Total Charge (coulombs)		
		Top	Bottom	Average*
L	--	1674	1010	1342
LF1(15)	15	537	360	448
LF2(15)	15	618	430	524
LF3(15)	15	513	328	841
LC1(15)	15	1245	681	963
LC2(15)	15	974	299	636
LF1(25)	25	387	209	298
LF2(25)	25	469	284	376
LF3(25)	25	326	270	298
LC1(25)	25	918	330	624
LC2(25)	25	605	264	434
S	--	1367	871	1119
SF1(15)	15	455	342	398
SF2(15)	15	831	471	651
SF3(15)	15	687	343	515
SC1(15)	15	1151	580	865
SC2(15)	15	1290	812	1051
SF1(25)	25	322	262	292
SF2(25)	25	473	302	388
SF3(25)	25	360	192	276
SC1(25)	25	614	391	502
SC2(25)	25	431	394	412

* Averages are given for comparative purposes. They are not reliable indicators, since values for top and bottom slices are so different.

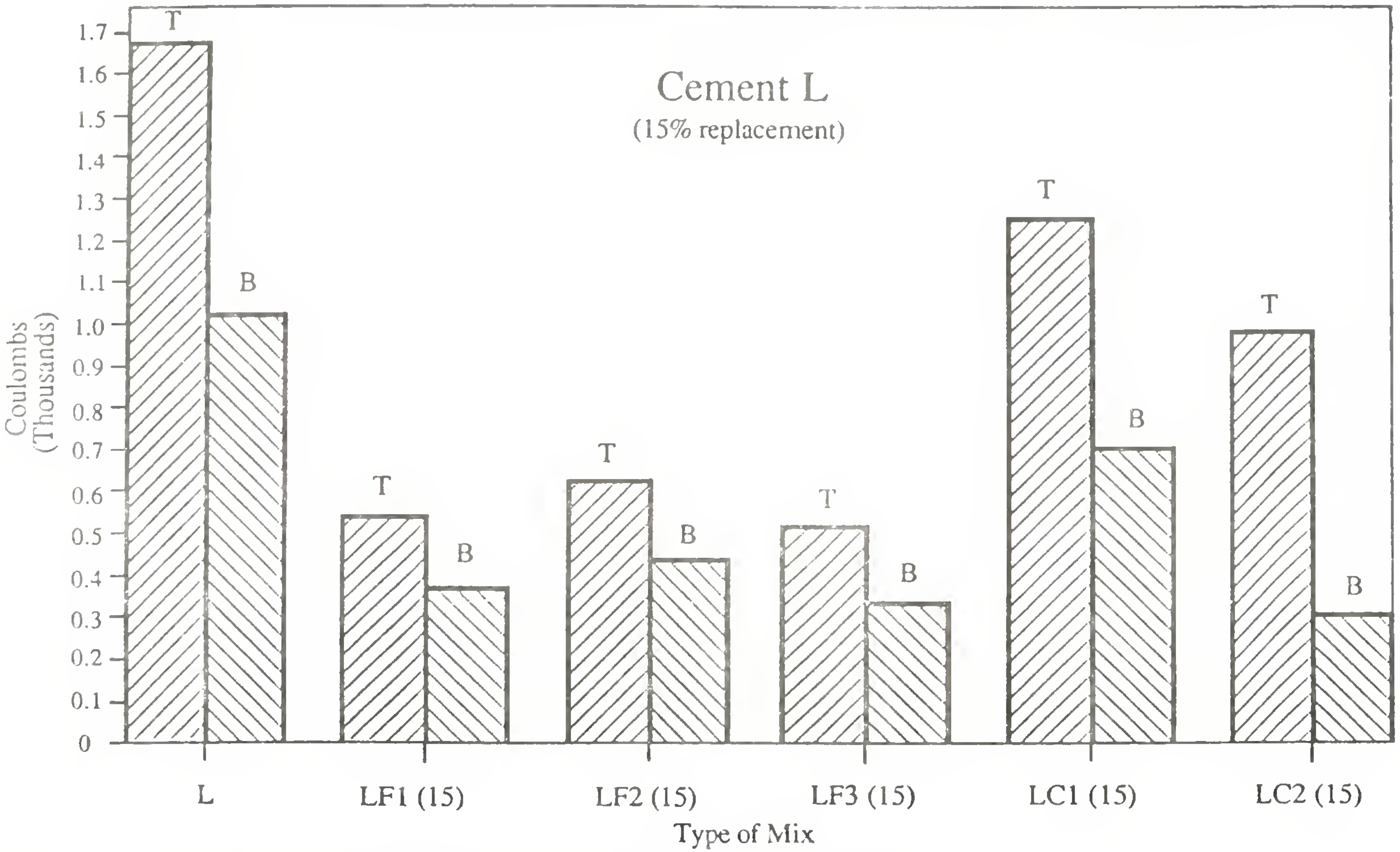

Figure 10.2-1 Charge passed during the chloride permeability test, (cement L, 15% replacement)

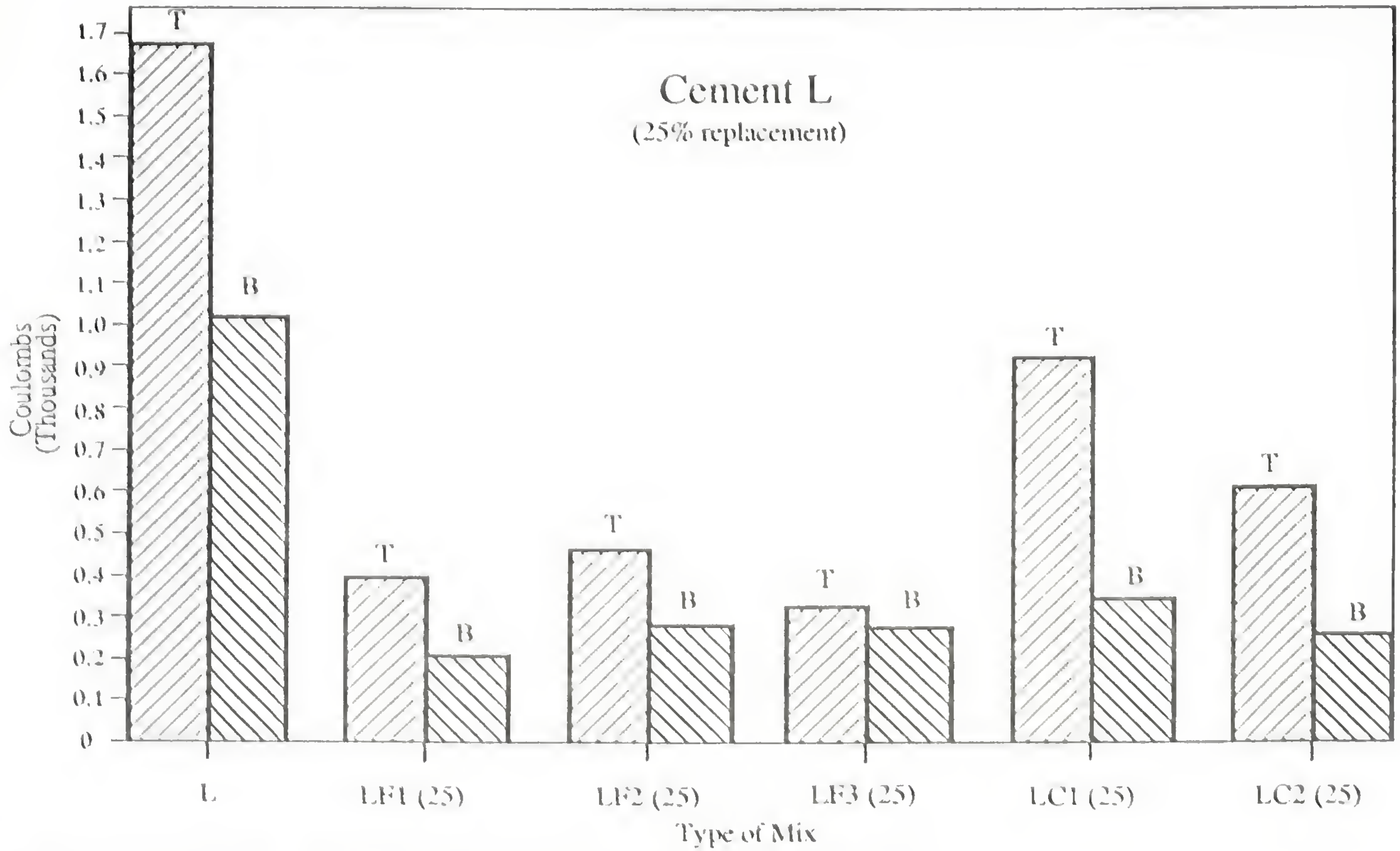

Figure 10.2-2 Charge passed during the chloride permeability test, (cement L, 25% replacement)

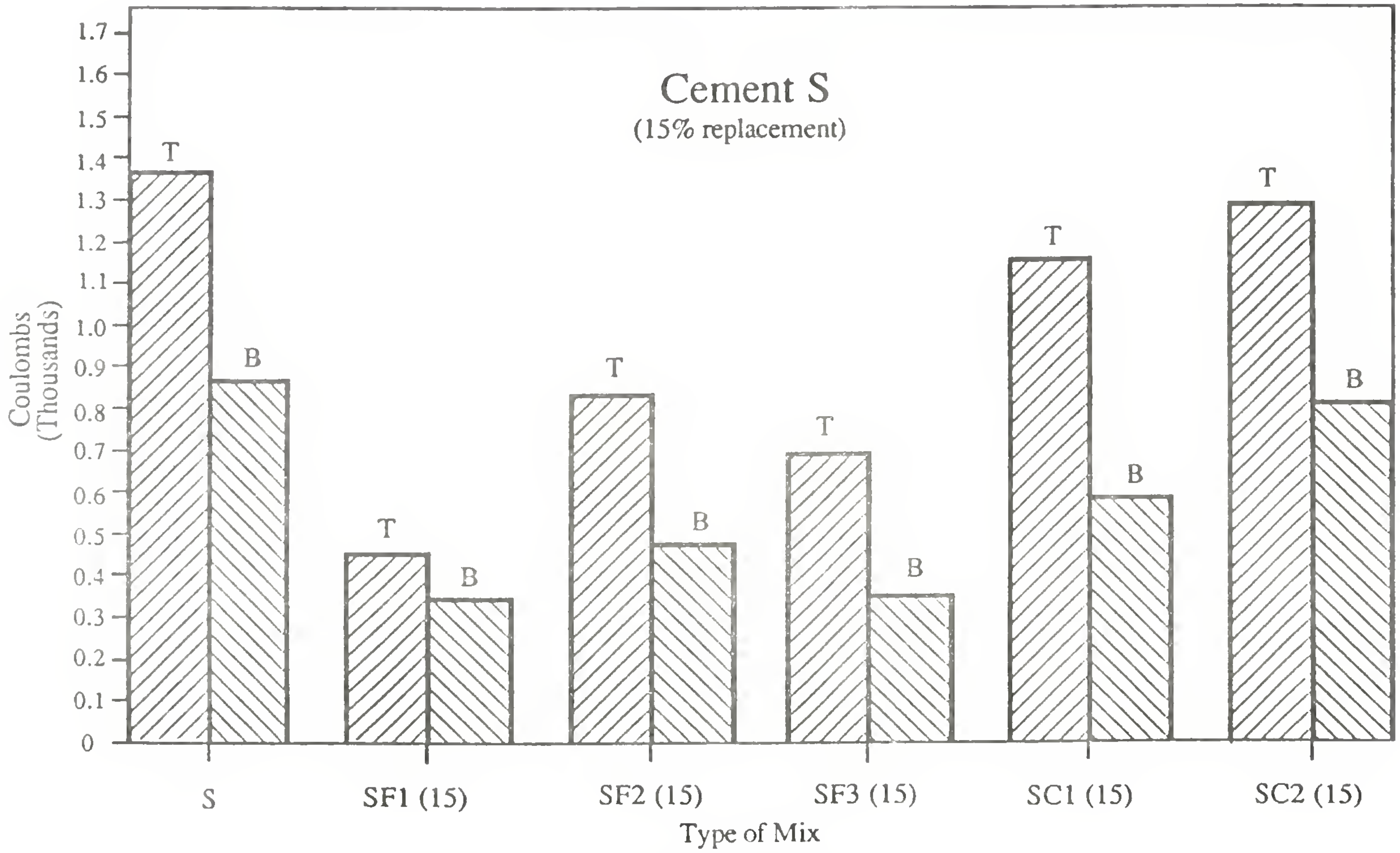

Figure 10.2-3 Charge passed during the chloride permeability test, (cement S, 15% replacement)

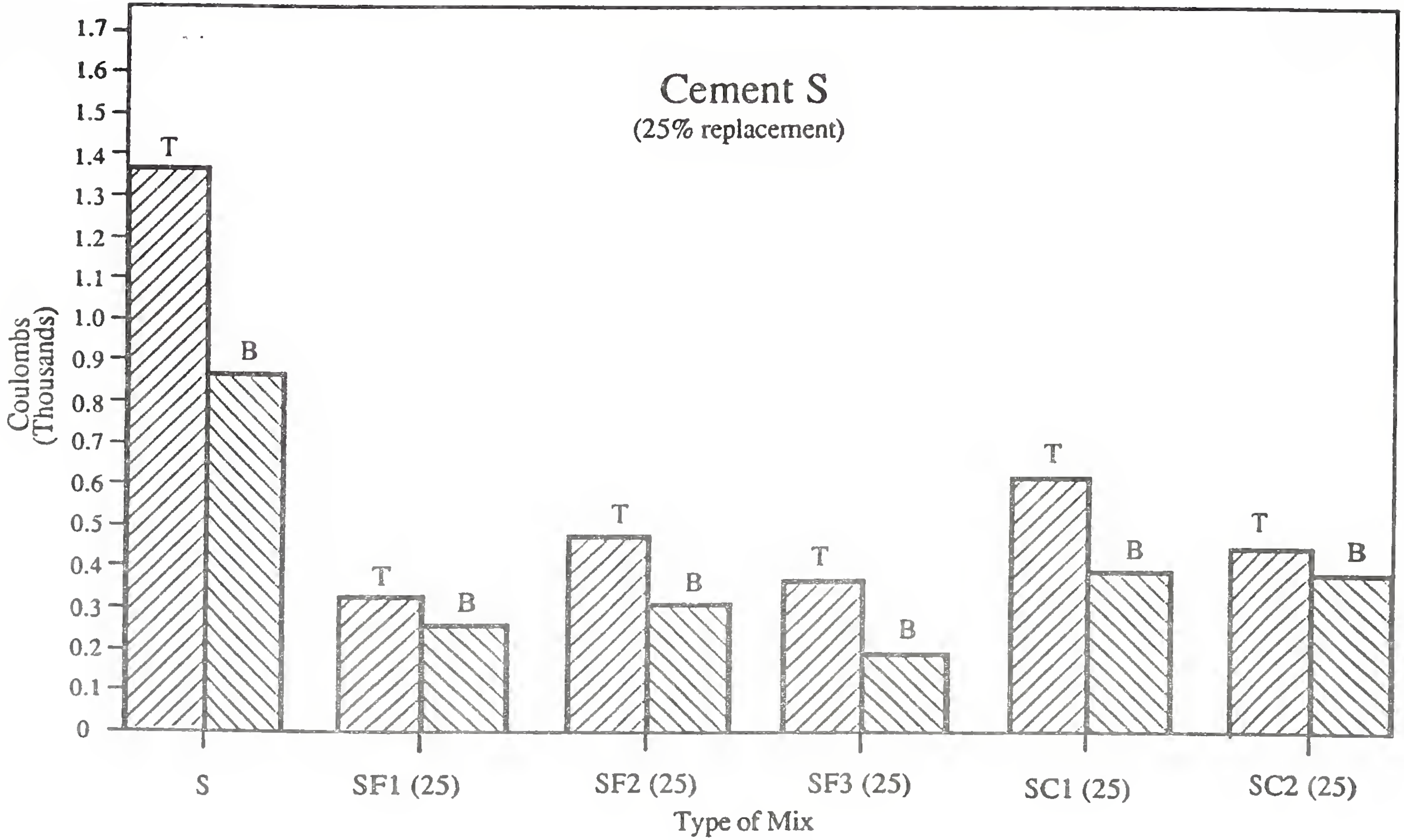

Figure 10.2-4 Charge passed during the chloride permeability test, (cement S, 25% replacement)

the parameters that influence strength are important in controlling the chloride permeability measurement.

Two mechanisms have been suggested as having major influence on the chloride permeability. Clogging of pores by gel produced from pozzolanic reaction has been indicated as one of the possible limiting mechanisms [219]. The effect of fly ash on the composition of the concrete pore solution has also been considered to be important [219,220], especially the concept that decreased concentrations of Na^+, K^+, and OH^- ions in fly ash concrete pore solutions may reduce the mobility of chloride ions.

As stated previously, in the present results it was found that the F1 fly ash resulted in the largest reduction in measured chloride permeability. This fly ash has a considerable content of exceptionally fine particles, which could lead to a greater degree of reaction in the concrete and production of larger amounts of C-S-H gel.

Generally speaking, despite the reductions in measured chloride permeability resulting from the fly ash addition, all of the concretes including both the reference plain concretes performed relatively well in this test. Using the AASHTO evaluation criteria, the plain concretes and concretes containing high calcium fly ash at 15% replacement level are all classified as having "low" chloride permeability (total charge ranging from 1000 to 2000 coulombs). All of the concretes containing low calcium fly ashes fall into the "very low" chloride permeability group (total charge ranging from 100 to 1000 coulombs).

10.3 Freezing and Thawing Resistance of Fly Ash Concrete

As described in Section 4.9.6, the ASTM C 666 [4] standard procedure B (freezing in air and thawing in water) was used to test the resistance of concretes to freezing and thawing. In this test the fundamental transverse frequency of the sample is measured before the first freezing cycle, and then repeatedly after approximately every 30 cycles of freezing and thawing. Any reduction in value of the fundamental transverse frequency indicates deterioration in the internal structure of concrete due to the frost action, and the extent of the reduction serves as an index of the extent of deterioration.

In these tests frequency readings were taken on 3 samples of each concrete after 0, 33, 55, 77, 111, 133, 154, 187, 220, 244, 268 and 303 cycles of freezing and thawing. The fundamental transverse frequencies measured were used to calculate the relative dynamic modulus of elasticity (P_c) according to the following formula:

$$P_c = (n_1{}^2/n^2) \times 100$$

where:

P_c = relative dynamic modulus of elasticity, after c cycles of freezing and thawing, in percent;

n = fundamental transverse frequency at 0 cycles of freezing and thawing;

n_1 = fundamental transverse frequency after c cycles of freezing and thawing.

Calculation of P_c assumes that the weight and dimensions of the specimen remain constant throughout the test. Since the weight of the specimens in this study never varied more than 1% over the 300 cycle test, this assumption was fulfilled.

ASTM C 666 requires that the investigator "continue each specimen in the test until it has been subjected to 300 cycles or until its relative dynamic modulus of elasticity reaches 60 percent of the initial modulus, whichever occurs first". The durability is than assessed by calculating the durability factor (DF) using the expression:

$$DF = PN/M$$

where:

DF = durability factor of the test specimen,

P = relative dynamic modulus of elasticity at N cycles, percent,

N = number of cycles at which P reaches the specified minimum value for discontinuing the test or the specified number of cycles at which the exposure is to be terminated, whichever is less, and

M = specified number of cycles at which the exposure is to be terminated.

Since all of the specimens performed well enough for the test program to continue to 300 cycles, the values of N and M are equal. In other words, the relative dynamic modulus of elasticity (P_c) at 300 cycles is identical to the durability factor (DF).

The durability factors obtained are given in Tables 10.3-1 to 10.3-4. Each number in these tables is an average based on data obtained for three different samples from the same batch of concrete. The results are also shown graphically in Figures 10.3-1 through 10.3-4.

It appears that all of the concretes made with either cement, any of the fly ashes, and at both 15% and 25% replacement levels, exhibited good durability as normally defined in interpreting the results of C 666 testing. The indicated durability factors at 300 cycles were all between 71 and 85 percent. These durability factors are thus relatively high, and are all within a narrow band, This suggests that all of the concretes had good air bubble systems in place, and that all were strong enough to resist freezing stresses.

The indicated durability results for the fly ash concretes are entirely similar to these for the reference plain portland cement concretes made with same cements.

One of the original objectives of this study was to provide a design procedure for obtaining durable fly ash concrete. The durability factor results presented in this section prove that this objective was satisfied with respect to indicated freeze-thaw durability.

In addition to the numerical results of the durability factor measurement, visual assessment of the physical appearance of all of the specimens was carried out. This confirmed that no damage of any type appeared that could be observed visually on the surface of any of the them, even after 300 cycles of freezing and thawing.

Finally, each of the bars were weighed at each evaluation, and

Table 10.3-1 The average values of durability factor and density of concrete, (cement L, 15% replacement).

	Mix					
	L	LF1(15)	LF2(15)	LF3(15)	LC1(15)	LC2(15)
Initial density (at 0 cycles) [lbs/cu ft]	147.05	148.87	147.78	146.33	149.88	149.60
Final density (after 303 cycles) [lbs/cu ft]	146.56	148.49	147.03	145.69	149.43	149.18
Number of cycles	Relative modulus (durability factor) [%]					
0	100.0	100.0	100.0	100.0	100.0	100.0
33	97.8	98.2	97.2	97.5	95.7	97.0
55	97.2	97.7	96.5	97.0	95.6	95.9
77	97.0	96.4	97.0	96.3	95.6	95.1
111	95.7	97.0	95.2	95.7	94.6	94.8
133	95.4	95.9	94.3	95.5	91.6	93.2
154	95.7	93.8	92.7	94.8	87.9	90.6
187	92.2	91.4	89.6	94.0	89.0	88.7
220	89.5	90.1	85.3	90.6	86.2	81.1
244	84.7	88.6	83.7	89.5	84.5	79.9
268	82.0	87.7	82.2	87.7	83.5	78.4
303	75.4	77.6	73.9	81.0	77.2	73.2

Table 10.3-2 The average values of durability factor and density of concrete, (cement L, 25% replacement).

	Mix					
	L	LF1(25)	LF2(25)	LF3(25)	LC1(25)	LC2(25)
	Initial density (at 0 cycles) [lbs/cu ft]					
	147.05	150.14	150.12	147.77	150.37	150.11
	Final density (after 303 cycles) [lbs/cu ft]					
	146.56	149.56	149.78	147.52	149.03	149.87
Number of cycles	Relative modulus (durability factor) [%]					
0	100.0	100.0	100.0	100.0	100.0	100.0
33	97.8	95.9	93.9	97.1	97.3	96.2
55	97.2	95.0	93.2	96.1	96.8	95.7
77	97.0	95.0	92.8	95.7	96.6	95.3
111	95.7	93.0	92.8	96.0	96.4	95.2
133	95.4	92.3	91.3	94.5	96.9	94.8
154	95.7	91.3	89.6	92.3	96.6	94.8
187	92.2	90.6	87.8	91.3	95.0	92.0
220	89.5	86.0	84.1	90.1	92.7	88.0
244	84.7	86.1	81.4	88.4	91.2	86.6
268	82.0	81.2	78.4	84.5	88.0	84.4
303	75.4	77.7	71.2	77.6	83.1	78.7

Table 10.3-3 The average values of durability factor and density of concrete, (cement S, 15% replacement).

	Mix					
	S	SF1(15)	SF2(15)	SF3(15)	SC1(15)	SC2(15)
Initial density (at 0 cycles) [lbs/cu ft]						
	146.78	145.30	147.76	146.48	148.17	147.94
Final density (after 303 cycles) [lbs/cu ft]						
	146.23	144.49	147.19	145.92	147.54	147.59
Number of cycles	Relative modulus (durability factor) [%]					
0	100.0	100.0	100.0	100.0	100.0	100.0
33	98.4	95.2	96.5	96.7	96.8	98.7
55	96.6	95.2	96.4	94.7	96.2	97.8
77	96.1	95.0	96.6	93.1	96.1	97.7
111	95.2	94.2	95.8	88.3	95.4	97.7
133	95.4	95.0	95.5	92.5	95.6	96.0
154	93.6	93.8	94.2	90.4	94.9	94.7
187	91.6	92.7	93.6	90.0	93.7	93.8
220	90.8	89.4	92.1	88.4	91.4	92.1
244	87.8	88.9	90.5	86.6	89.3	90.4
268	86.8	90.2	86.8	85.3	86.5	88.2
303	81.8	79.7	81.2	82.2	79.9	82.2

Table 10.3-4 The average values of durability factor and density of concrete, (cement S, 25% replacement).

	Mix					
	S	SF1(25)	SF2(25)	SF3(25)	SC1(25)	SC2(25)
	Initial density (at 0 cycles) [lbs/cu ft]					
	146.78	144.88	146.64	149.05	149.47	149.27
	Final density (after 303 cycles) [lbs/cu ft]					
	146.23	144.22	146.01	148.72	149.00	148.15
Number of cycles	Relative modulus (durability factor) [%]					
0	100.0	100.0	100.0	100.0	100.0	100.0
33	98.4	96.4	97.9	94.7	94.0	96.4
55	96.6	96.5	94.8	94.8	92.6	95.6
77	96.1	95.5	94.0	93.0	93.0	96.0
111	95.2	95.1	94.3	93.1	92.7	93.4
133	95.4	95.8	93.4	91.8	90.8	92.5
154	93.6	95.4	92.4	91.8	90.2	90.4
187	91.6	93.8	90.0	91.3	89.3	89.6
220	80.8	93.4	88.3	91.0	86.5	88.4
244	87.8	93.3	88.1	90.0	84.7	85.1
268	86.7	89.9	87.0	87.9	85.3	82.0
303	81.8	84.6	80.7	83.2	82.6	78.0

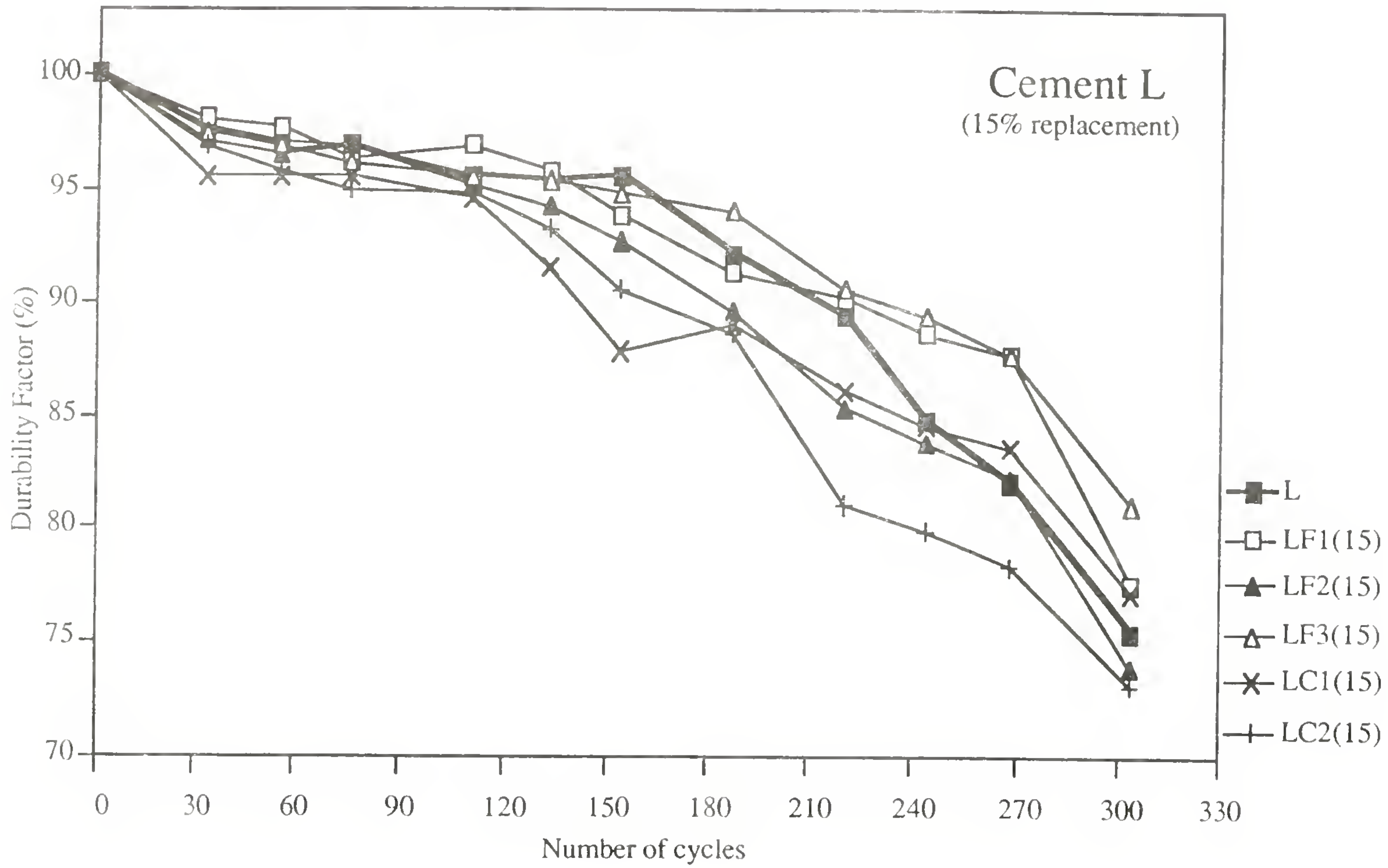

Figure 10.3-1 Durability factor vs. number of freezing and thawing cycles, (cement L, 15% replacement).

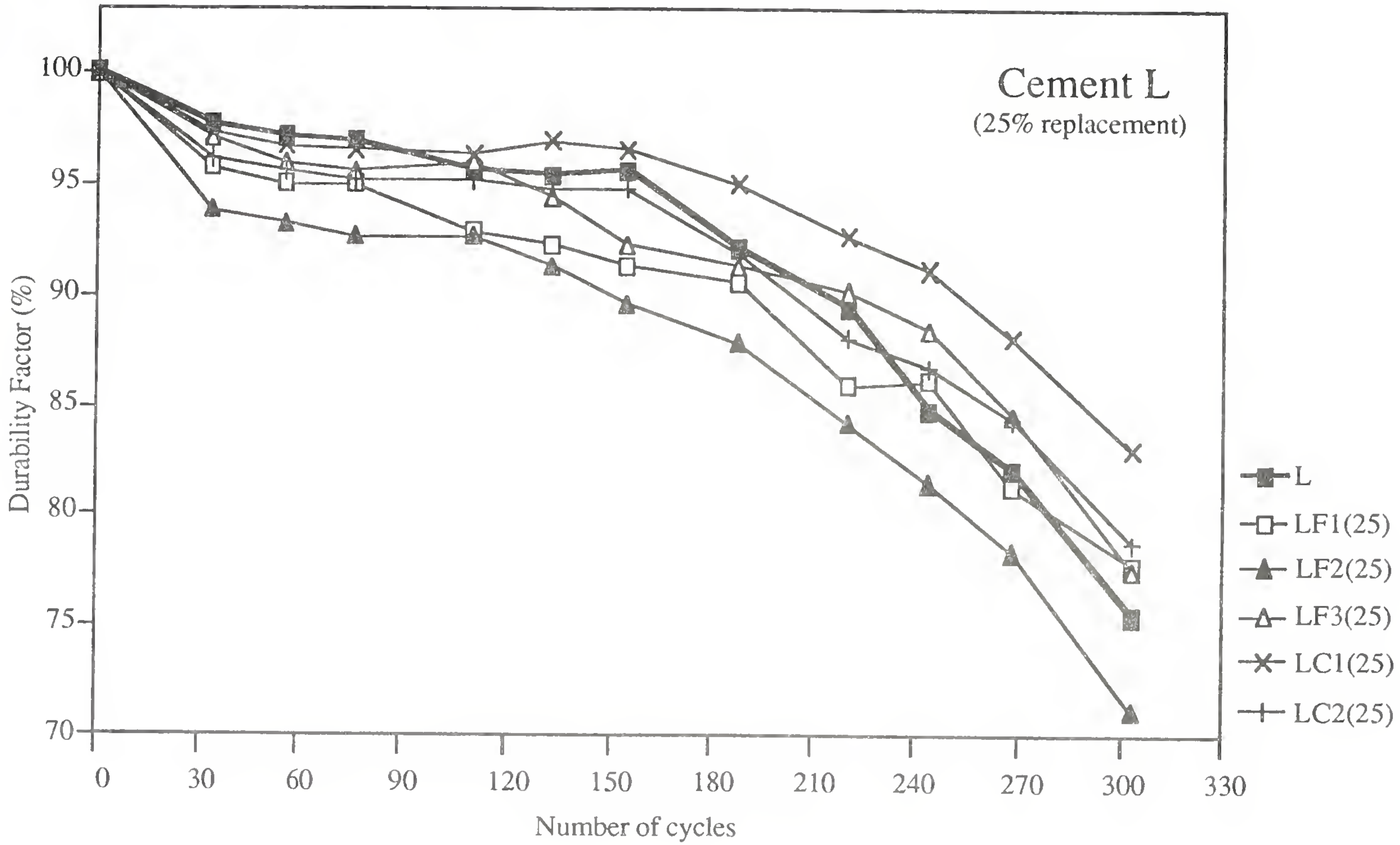

Figure 10.3-2 Durability factor vs. number of freezing and thawing cycles, (cement L, 25% replacement).

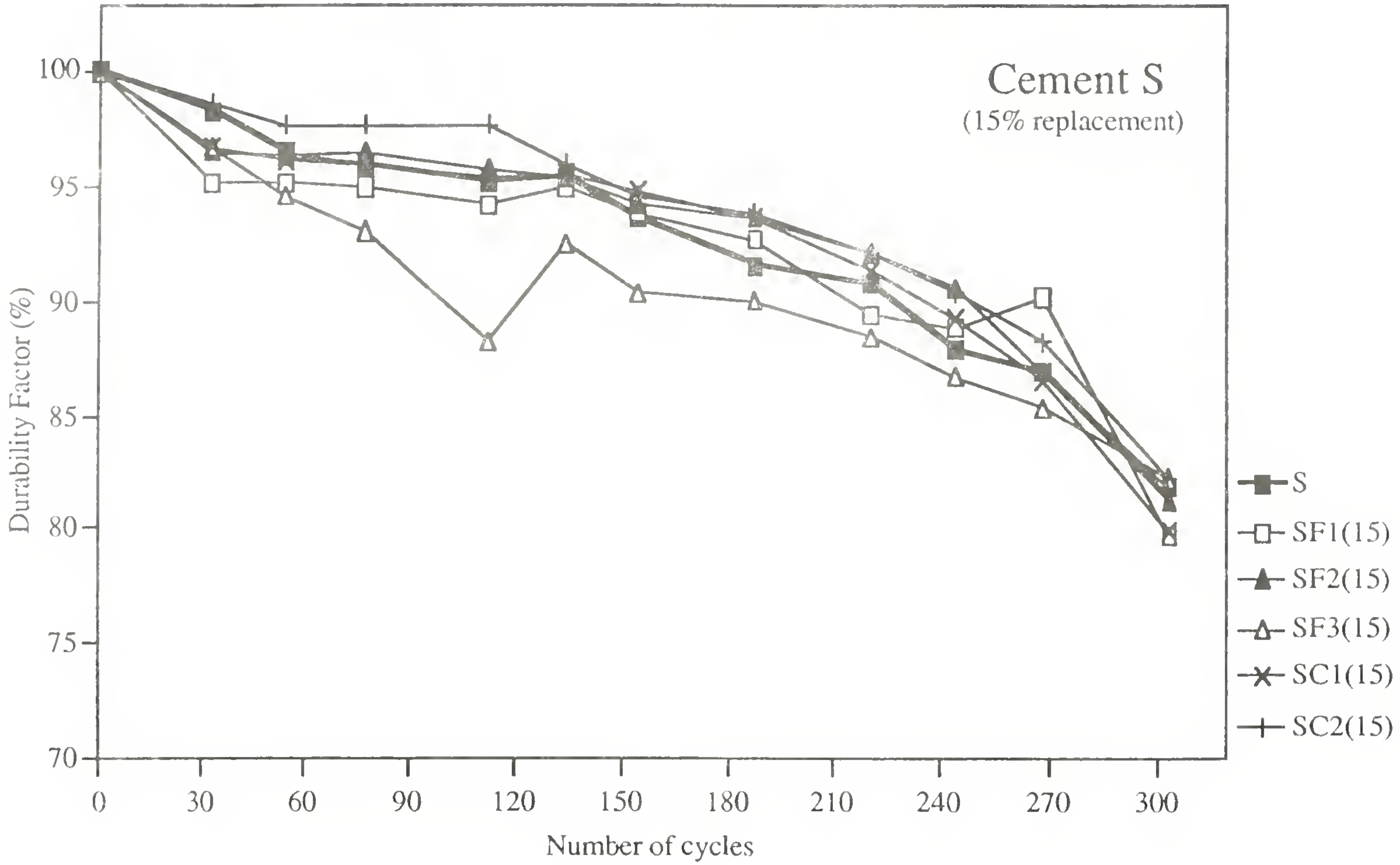

Figure 10.3-3 Durability factor vs. number of freezing and thawing cycles, (cement S, 15% replacement).

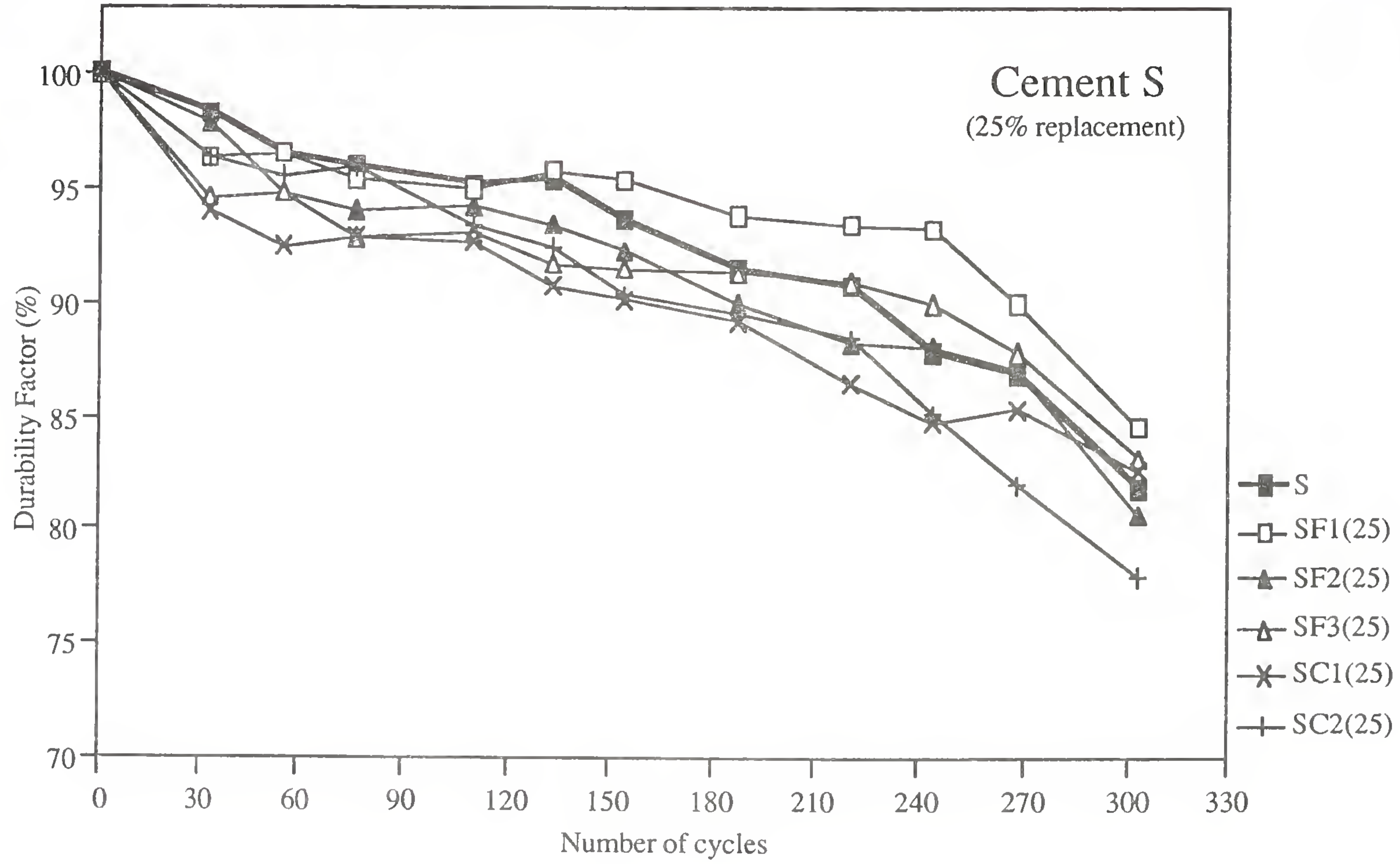

Figure 10.3-4 Durability factor vs. number of freezing and thawing cycles, (cement S, 25% replacement).

the resulting measurements of density are included in Tables 10.3-1 through 10.3-4. The very small changes in measured densities in the course of the 300 cycles of freezing and thawing additionally confirm that little damage has taken place.

It may be concluded from the above findings that type and the amount of fly ash are not significant factors in influencing the freeze-thaw resistance of the concrete, providing the designer is aware of the possible influence of the fly ash on the amount of air-entraining agent needed and takes the necessary steps to insure a proper air bubble system. If a properly entrained air void system is produced in the concrete, and assuming that the aggregate is not itself susceptible to freezing damage, properly designed fly ash concrete should always be durable to freezing and thawing.

10.4 Durability-Related Pore Solution Parameters

The pore solution in plain portland cement concrete has been shown many times to consist primarily of an aqueous solution of concentrated alkali hydroxides, the concentration being a function of the alkali content of the cement and the mix design (i.e. the water:cement ratio). The resistance of concrete to corrosion depends on a passivating oxide film that depends on a high concentration of OH^- ions for its maintenance, especially if an chlorides are introduced into the concrete. However, maintenance of a high concentration of OH^- ions in the pores solution may not be an unmixed blessing; it accentuates the possibility of alkali aggregate attack should marginally susceptible aggregate be present.

The influence of fly ash on the concentration of OH^- ions in long-term concrete pore solutions is thus an important potential parameter related to its durability.

Measurements were carried out in this study of the concentrations of potassium, sodium, calcium, SO_4^{2-} and OH^- ions in the pore solutions of cement pastes made up so as to be of the same composition as the concretes studied, but without the aggregate. Pastes were made up using cement L, and cement L with each of the fly ashes at the 25% replacement level. These pastes were sealed and allowed to hydrate for approximately 7 months (actual ages between 209 and 217 days) before the pore solution was removed by special high pressure apparatus and the solutions were analyzed.

The results are given in Table 10.4-1.

Table 10.4-1 Results of Pore Solution Analyses

	Concentration, Equivalents/Liter					
Paste	OH^-	SO_4^{2-}	K^+	Na^+	Sum($^-$)	Sum($^+$)
L	0.548	0.012	0.481	0.078	0.560	0.559
LF1(25)	0.345	0.005	0.271	0.078	0.350	0.349
LF2(25)	0.344	0.006	0.302	0.070	0.350	0.372
LF3(25)	0.389	0.008	0.292	0.104	0.397	0.396
LC1(25)	0.520	0.007	0.157	0.363	0.527	0.520
LC2(25)	0.499	0.006	0.297	0.191	0.505	0.488

In Table 10.4-1 we provide the individual analysis results (in equivalents/liter, i.e. normality) for the OH^- and SO_4^{2-} anions and the K^+ and Na^+ cations. The only other ion normally present is Ca^{2+}, but previous experience has indicated that its concentration level in mature cement pastes rarely exceeds 0.001N, and it was not analyzed for.

The last two columns give the sums for the concentrations of anions and for cations; these should check each other within analytical error. The results for all of the solutions are within reasonable closeness, and for three of them are within 0.001 N.

The results indicate that incorporation of the fly ashes can have a pronounced effect on the long-term solution characteristics.

The effect of most significance is on the OH^- ion concentration. The value for the reference cement paste is about 0.55 N; this is reduced to between 0.34 and 0.39 N for the low calcium fly ash pastes, i.e. a reduction of 29% to 37%. In these mixes, the weight proportion of cement to water is reduced only 20% compared to the reference paste, so that it is evident that the low calcium fly ashes are actively removing OH^- ions from solution.

For the high calcium fly ashes, the OH^- ion concentrations are about 0.50 and 0.52, respectively, much closer to that of the reference cement paste. In fact, these values are higher than 80% of the reference paste value (0.44N), suggesting that the Class C fly ashes are contributing to the effective alkalinity, although not by as much as the cement that they are replacing.

These results indicate that the Class F fly ashes tested here result in pore solution changes that are highly favorable with respect to possible alkali-aggregate reaction, but perhaps unfavorable with respect to the "alkalinity reserve" against steel corrosion should chloride be allowed to penetrate the concrete. The Class C fly ashes have much less effect either way, since they change the OH^- ion concentration only modestly.

It is also instructive to examine the separate concentrations of K^+ and Na^+ ions reported in the analyses. The solutions are all essentially potassium and sodium hydroxide solutions, with the OH^- effectively balancing the sum of the alkali ions, but as seen in the table, the fly ashes affect the concentrations of the two alkali ions differently. This is brought out more clearly in Figure 10.4-1, in which the alkali ion concentrations for the reference cement and for each fly ash paste are plotted individually.

The pore solution for the portland cement past (PC) is shown to have about 5 times as much K^+ as Na^+, reflecting the differing amounts of the two element in composition of the portland cement itself. It is seen in the figure that for both F1 and F2 fly ashes, the Na^+ concentration is unchanged; that is, the reduction in alkalinity induced by these fly ashes reflects almost entirely a lowering of the K^+ content. For fly ash F3, there is actually an increase in the Na^+ ion concentration, but this is more than balanced by the major decrease in the K^+ content.

This tendency is even more pronounced for the high calcium fly ashes. For C1 the Na^+concentration is more than twice what it is for the reference cement paste, and the reduction in K^+ content is not so severe. The explanation appears to be that this fly ash is actively releasing Na^+ ions as it reacts with the cement. An even stronger response of the same kind is shown for fly ash C2, where the Na^+

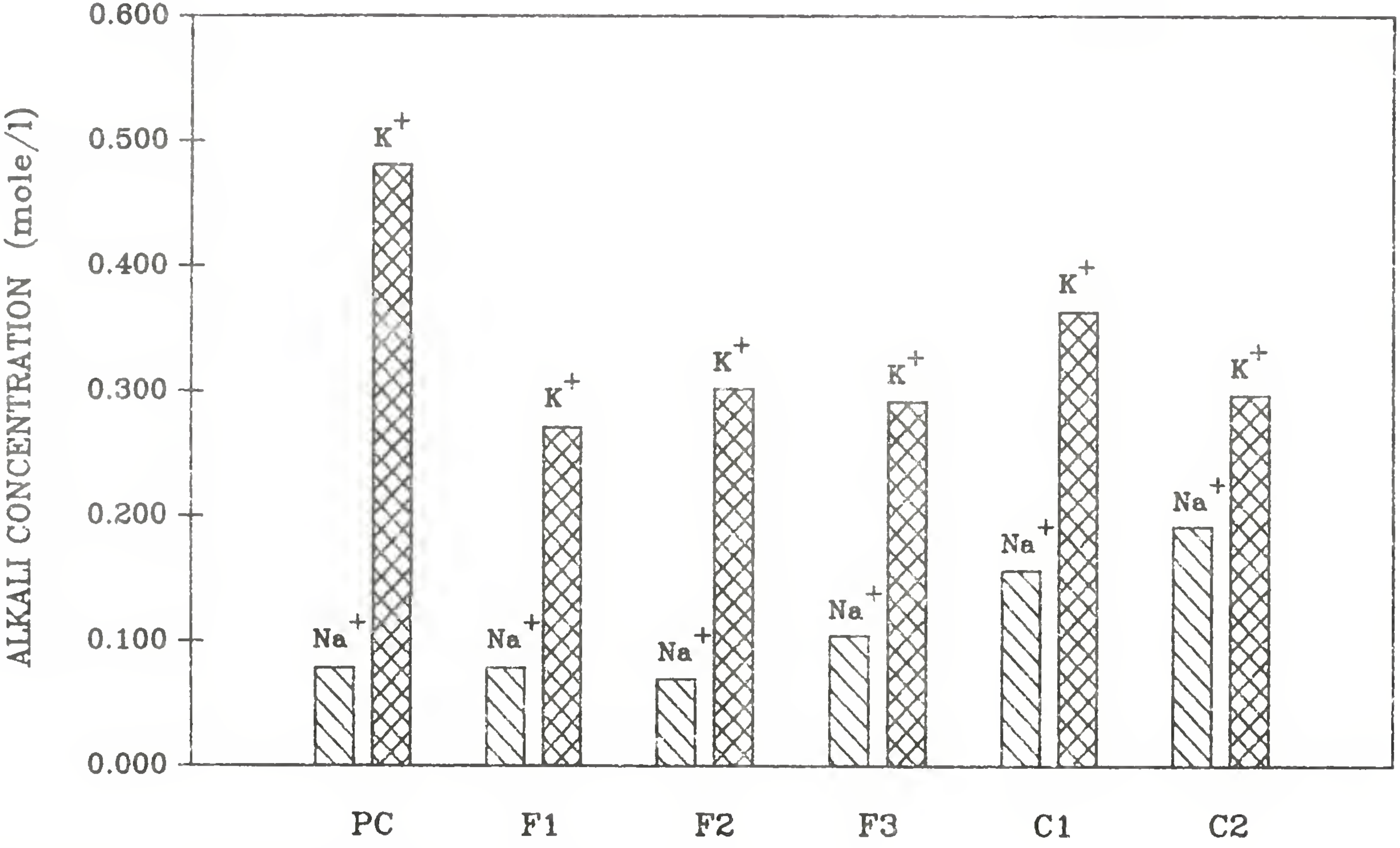

Figure 10.4-1 Pore solution alkali concentrations in mole/liter.

concentration is almost 2-1/2 times what it is in the reference cement paste.

In general, it appears that (1) the low calcium fly ashes reduce the alkalinity of the pore solution significantly by removing potassium ions, (2) the high calcium fly ashes reduce the alkalinity only moderately, by removing less potassium and by actively releasing considerable amounts of sodium into the solution. As a result, the Na:K balance in the solution changes over that of the portland cement, moderately for the Class F ashes and strongly for the Class C ashes. It is not known with any certainty whether or not the changes in the relative amounts of two the alkali ions would have any effect on whether corrosion or alkali aggregate attack problems.

Finally, it should be recorded that the SO_4^{2-} ion concentrations found were all low, but did appear to be influenced by the fly ash. The value was 0.012 N for the reference cement paste, and this was reduced to between 0.005 N and 0.008 N for the fly ash pastes. There seemed to be little difference between effects of the Class F and Class C fly ashes in this regard.

10.5 Effects of Fly Ashes on Pore Solution Chloride Ion Concentration

One of the possible influences of fly ash incorporation on concrete durability involves a possible interaction of the fly ash with chloride ions either deliberately included in the concrete mix, or penetrating into concrete from outside. The potential for steel corrosion is very much enhanced by the presence of dissolved chloride ions in the pore solution in contact with reinforcing steel, and the use of chloride-containing admixtures such as calcium chloride is discouraged for this reason.

Experience has shown that if chloride is incorporated in the mix, a considerable proportion of it may be tied up in a form of calcium aluminate chloride hydrate (Friedel's salt), or in calcium silicate hydrates, and so inactivated. The proportion that is so bound depends on the dosage level introduced, and also on the particular cement used.

The effect of fly ash on this process of inactivating chloride is a subject of considerable current concern, especially where either chloride-containing admixtures may be used, or as in the case of bridge deck and highway pavement concrete, salt application is a common feature of the service environment.

It is thus of interest to establish the potential effectiveness of different fly ashes in contributing to this inactivation process. While it has already been shown in Section 10.2 that the presence of fly ash significantly reduces the chloride permeability, the fact remains that chloride ions eventually will penetrate to the level of steel in many potential field exposures of fly ash concrete in highways.

Accordingly, pastes of cement L and of cement L and each of the fly ashes were batched at the 25% replacement level, using the standard w:(c+fa) ratio of 0.49. These pastes were different from those previously examined in that a weight of calcium chloride equivalent to 1% of the weight of the original cement batch was dissolved in the mix water of each. The pastes were cast into molds, sealed, and cured for approximately three months (actually, 86 days). Pore solutions were then pressed out of each of the pastes and analyzed for the residual concentration of chloride ions using the normal chloride specific ion electrode technique.

The results are given in Table 10.5-1.

Table 10.5-1 Results of Pore Solution Chloride Analyses

	Cl^- Concentration, Moles/Liter	Percentage of Initial Concentration
L	0.0849	23.2 %
LF1(25)	0.0435	11.9 %
LF2(25)	0.0431	11.8 %
LF3(25)	0.0562	15.4 %
LC1(25)	0.0296	8.1 %
LC2(25)	0.0343	9.4 %

Incorporation of each of the fly ashes resulted in further reductions of the concentration level of dissolved chloride. The low calcium fly ashes were less effective than the high calcium ones, but nevertheless reduced the chloride concentrations to the order of 12 to 15% of the initial value. The high calcium fly ashes resulted in levels of between 8% and 10% of the initial chloride concentration.

It is thus apparent that fly ash exerts a significant beneficial effect with respect to potential steel corrosion in concrete. Not only is the chloride permeability reduced significantly, but the capacity of cement for binding chloride so that it is inactive with respect to corrosion effects is significantly enhanced.

11.0 STUDIES OF REACTIVITY IN FLY ASH

Use of fly ash as a partial replacement for cement in concrete is possible only because of the chemical reactivity of the fly ash in the hydrating cement system. Conventionally, low calcium fly ashes are described as having the capacity to take part in "pozzolanic" reactions, i.e. to react with calcium hydroxide formed in earlier cement hydration processes, and high calcium fly ashes are described as being able to take part in both "pozzolanic" and "cementitious" reactions, i.e. reactions with water directly. Actually the situation is more complicated than this; the presence of even low calcium fly ash alters the cement hydration reactions, and changes both the reaction rates and the nature of the hydration products formed.

Regardless of the details, it is well understood that different fly ashes, of either class, vary in their reactivities in concrete. It is desirable to form some estimate, at least, of the relative reactivities of different fly ashes that may be used in a particular application.

We have carried out a number of studies aimed at different aspects of the problem of comparing the reactivities of different fly ashes, and of estimating the type and extent of reaction that has taken place in a given cement-fly ash paste. The results of these studies are provided in this chapter.

11.1 Pozzolanic Reactivity as Indicated by Residual Calcium Hydroxide Retention

The most direct measurement for the "pozzolanic reaction" that has taken place with a fly ash with a given cement is the content of calcium hydroxide that remains in the system after the period concerned, compared to that generated in the same period by the cement without fly ash, i.e. without the opportunity for pozzolanic reaction.

Portland cement hydrates to produce C-S-H gel and calcium hydroxide as its main hydration products. In the absence of fly ash, the amount of calcium hydroxide produced by the cement hydration reactions at a given age varies somewhat from cement to cement, depending mostly on the relative proportions of C_3S and C_2S present in that particular cement. The amount of calcium hydroxide generated per unit of C_3S that hydrates is three times that generated per unit of C_2S that hydrates, so that this is not a negligible variation. Thus, to gauge the degree of reaction with calcium hydroxide, one must first establish the amount of calcium hydroxide that would be present in the paste without fly ash, and then compare this to the presumably smaller amount that is left after the fly ash has had a chance to react with it.

In the present studies, pastes were prepared with cement L at the 0.49 w:c ratio used previously, and with cement L and each of the fly ashes at the 0.49% w:(c+fa) ratio and the 25% replacement level. The pastes were sealed and allowed to hydrate for periods ranging from 1 day through 180 days, dried, powdered, and examined by differential thermal analysis (DTA). The presence of calcium hydroxide is indicated by a peak at approximately 500 °C in this method.

A calibration was prepared using standard known mixtures of reagent grade calcium hydroxide and an inert powder. The peak area vs. percent calcium hydroxide relationship obtained was effectively linear. The peak areas for the calcium hydroxide peak of each of the pastes at each age were then measured, and the content of calcium hydroxide determined by reference to this calibration curve.

The results are given in Table 11.1-1, and shown schematically in Figures 11.1-1 through 11.1-3.

Table 11.1-1 Calcium Hydroxide Contents of Cement Pastes And Fly Ash - Cement Pastes At Various Ages

	Calcium Hydroxide Content, % by Weight					
Paste	1 day	3 days	7 days	28 days	90 days	180 days
L	11.3	13.7	15.3	14.9	16.3	15.7
LF1(25)	9.8	11.0	12.2	12.3	12.1	11.2
LF2(25)	9.5	11.5	12.1	11.9	12.3	11.4
LF3(25)	9.3	11.1	11.5	11.9	10.4	11.6
LC1(25)	10.7	12.8	13.3	13.0	13.3	11.9
LC2(25)	8.2	11.3	11.8	11.1	11.8	11.4

The evidence of this data concerning reactivity of the fly ashes is not accord with the usual ideas of pozzolanic reaction of fly ash in concrete.

Fig. 11.1-1 shows two plots of calcium hydroxide content as a function of time. The upper plot is the experimentally observed content of calcium hydroxide in cement paste L. The lower plot is

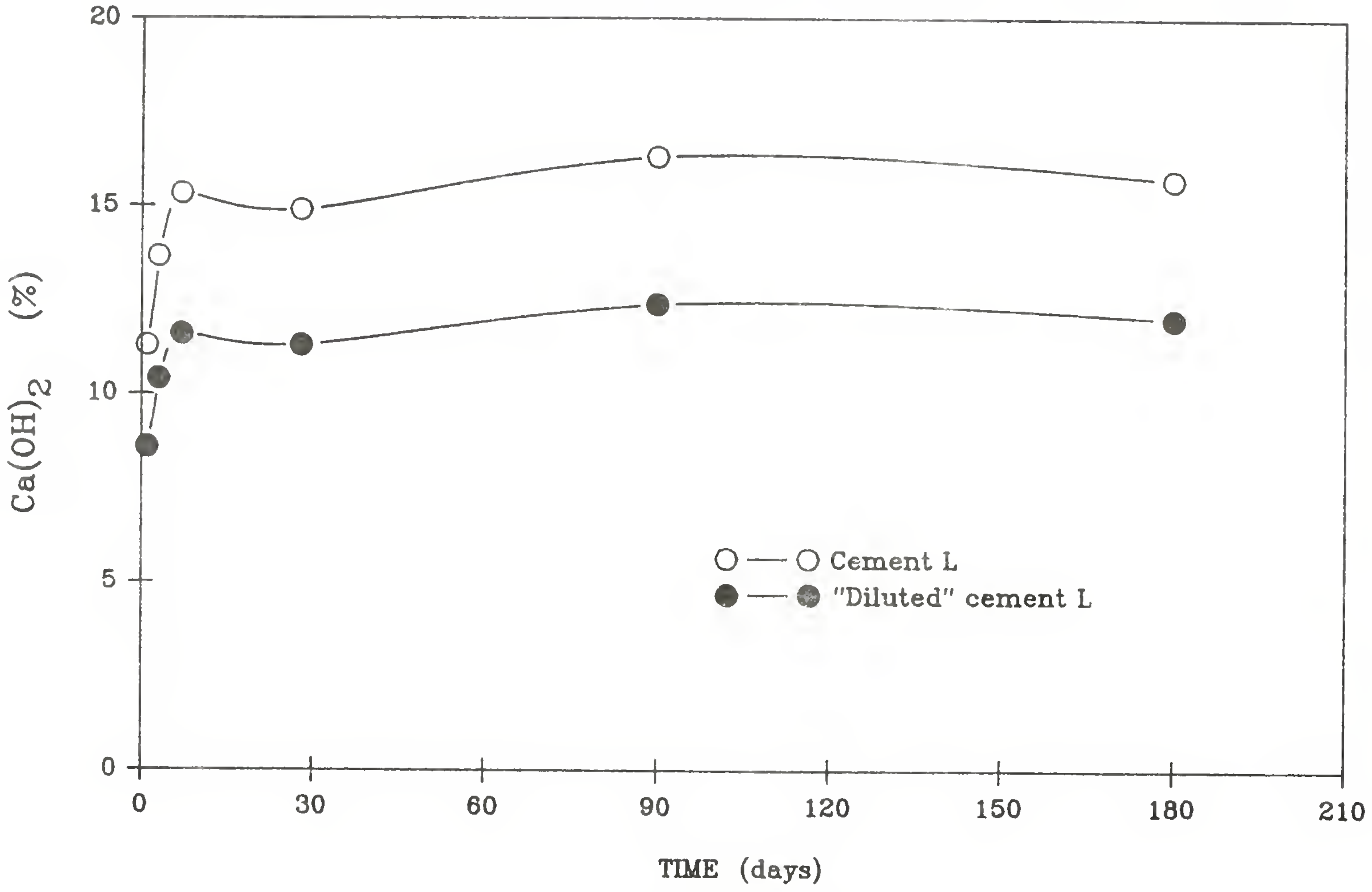

Figure 11.1-1 Calcium hydroxide content of L reference cement paste compared with these of "diluted cement paste" as a function of age.

derived from each value in the upper plot by multiplying it by the dilution factor for cement in the fly ash pastes. For every 100 g. of cement in the cement paste, there are 80 grams of cement in the fly ash paste mixes, to this, 25 grams of fly ash have been added. Thus the cement dilution factor in the starting fly ash pastes is 0.80/1.05, or 0.762.

The lower plot is composed of each point on the upper plot multiplied by this dilution factor.

The function of this "diluted cement" plot is to provide a basis of comparison for the results of the calcium hydroxide determinations in the fly ash pastes. In those paste, if there is no change in the way the portland cement hydrates, and if there is no consumption of calcium hydroxide by the pozzolanic reaction, we would expect no difference from the "diluted cement" line for calcium hydroxide content. Another way of putting it is that departures from this line indicated reactions taking place with the fly ash that influence the content of calcium hydroxide retained in the fly ash pastes.

Figure 11.1-2 shows a comparison of this "diluted cement" curve with calcium hydroxide contents determined at each age for the three low calcium fly ashes, F1, F2, and F3. The inescapable conclusions from this comparison are that (1) there seems to be no real difference between the calcium hydroxide contents at each age among the pastes containing the different low calcium fly ashes, and (2) there is no real difference between the calcium hydroxide contents of these fly ash pastes and that of the "diluted cement" curve at the same age. In other words, so far as these calcium hydroxide content measurements

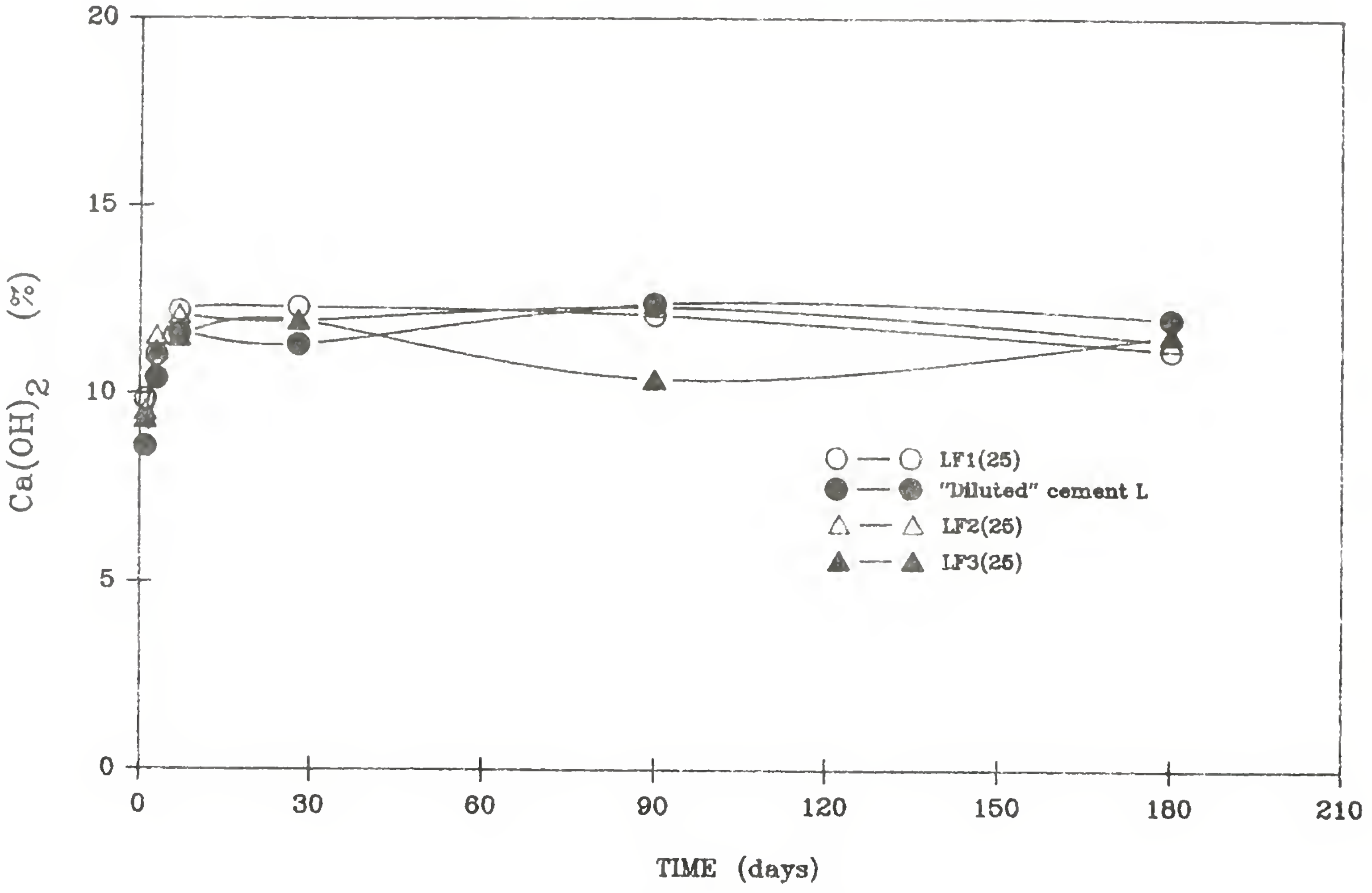

Figure 11.1-2 Calcium hydroxide contents of low calcium fly ash - bearing pastes compared with those of "diluted cement paste" as a function of age.

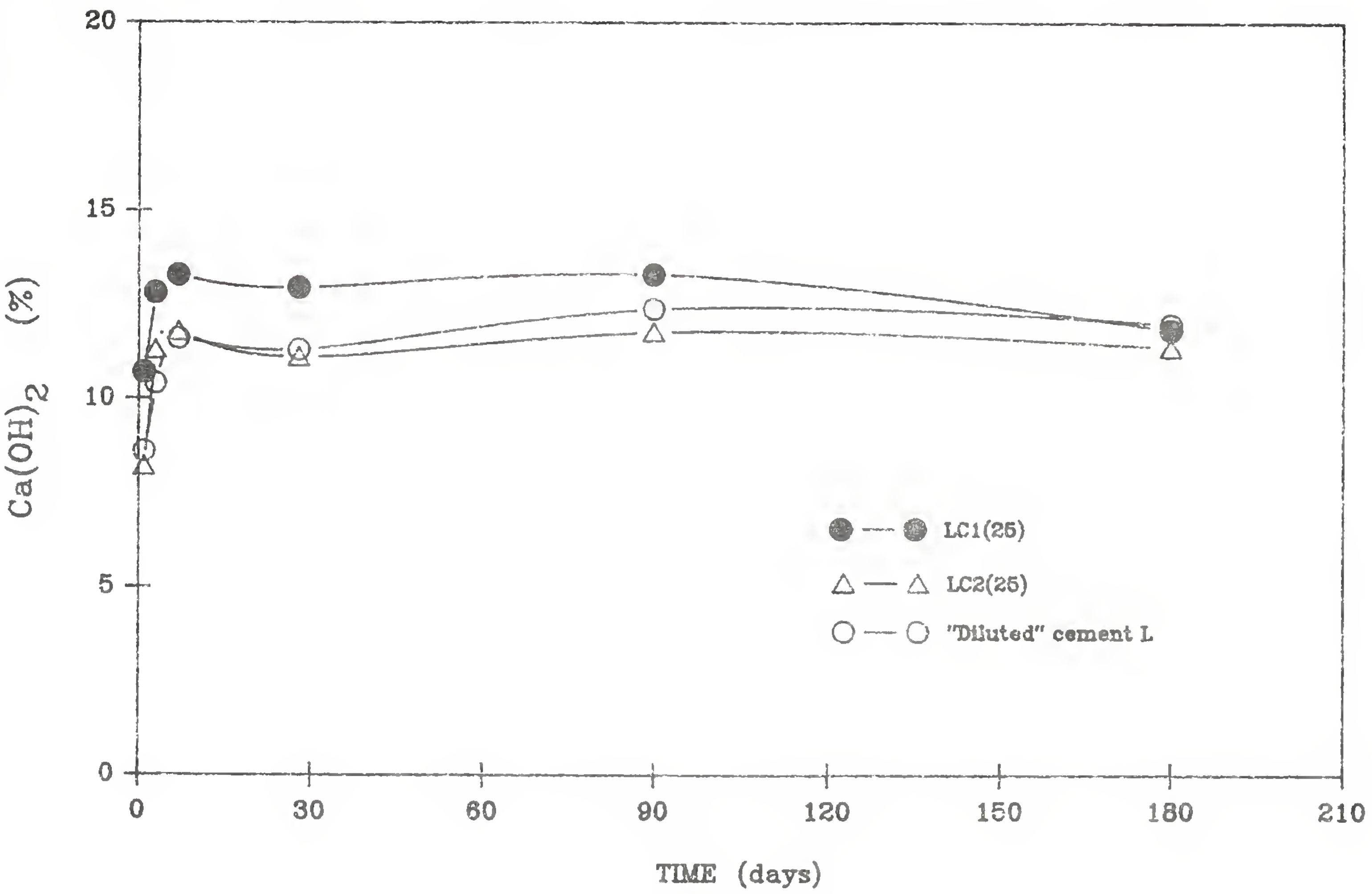

Figure 11.1-3 Calcium hydroxide contents of high calcium fly ash - bearing pastes compared with those of "diluted cement paste" as a function of age.

are concerned, there is no evidence for anything but a dilution effect from the incorporated fly ashes, and no real evidence for any "pozzolanic" reaction, even after 180 days.

Figure 11.1-3 shows a similar plot for the "diluted cement" curve and for curves for the two high calcium fly ashes. For the C1 pastes, there is clearly an augmentation of the calcium hydroxide content starting from the first day, and persisting to 90 days, but disappearing by 180 days. The implication is that extra calcium hydroxide is produced in this paste, presumably by rapid reaction of the free crystalline CaO contained in it with the mix water. The indication of the data is that this extra calcium hydroxide has been consumed, presumably by pozzolanic reaction, between 90 and 180 days.

The comparison for the C2 fly ash is different. There is no indication of any "extra" calcium hydroxide produced at any stage of the process. Neither is there any indication of a pozzolanic reaction removing any of the calcium hydroxide at any stage, the curve for the C2 paste being almost identical to that the hypothetical "diluted cement" at all of the ages examined.

These results are somewhat unexpected. If they are to be trusted, they suggest that the extra strength derived by fly ash concretes in ages between 28 days and 180 days, as has been demonstrated in Chapter 9, does not result from reaction with calcium hydroxide, as has been long assumed.

It also should be cautioned that the data extend only to 180 days. No direct evidence is available for pozzolanic reaction or lack of it, beyond this period.

11.2 Assessment of Reactivity from Non-Evaporable Water Content Measurement

The degree of hydration of a given cement at any given stage of reaction is often measured by a parameter called the "non-evaporable water content". This is a measurement of the water bound into cement hydration products formed during the hydration processes. As mentioned previously, the primary hydration products are C-S-H gel and calcium hydroxide, both of which contain substantial amounts of H_2O that is not evaporable under the usual drying conditions, but that can be driven off at higher temperatures. This constitutes the non-evaporable water. It is usually assumed that there is a linear relationship between the extent of cement hydration and the content of non-evaporable water accumulated in the paste or concrete.

In the usual determination of non-evaporable water content, the sample is first dried to a reference state, either by oven drying or by one of several available less rigorous drying procedures. The water lost at this stage is "evaporable". After weighing, the sample is then heated to ignition temperature, typically 750 °C or more, cooled, and reweighed. The weight loss recorded in this second step is the non-evaporable water. It is usually expressed as a percentage of the ignited weight, the latter quantity being the same as that of the original cement in the paste sample.

Experiments by various workers have indicated that most completely hydrated portland cements produce a non-evaporable water content value of approximately 22% by weight of ignited material. It is usually assumed that the effective degree of hydration for a given paste is linearly proportional to its measured non-evaporable water content. The method thus provides a relatively simple way to estimate the degree of hydration of the cement in a given material.

In the present research, non-evaporable water content measurements were made from samples of the same pastes discussed in Section 11.1, and at the same times. The pastes were oven dried at 105 °C overnight, weighed, and ignited to 1050 °C and reweighed to make these measurements. It was assumed that no carbonation had taken place.

The results for the cement paste are given in Table 11.2-1, which also provides the equivalent estimated degree of hydration as a function of age.

Table 11.2-1 Non-evaporable Water Contents of Reference Cement Paste And Corresponding Estimated Degree of Hydration

Paste	1 day	3 days	7 days	28 days	90 days	180 days
Nonevaporable H_2O %	11.2	14.2	16.6	17.7	18.7	17.9
Est. Degree of Hydr., %	51	66	75	80	85	81

The results suggest that the cement paste is a little less than half hydrated at 1 day, and is about 80% hydrated by 28 days; only a little additional hydration seems to have taken place beyond that time.

The corresponding results for the fly ash pastes are provided in

Table 11.2-2. Also included in this table is a calculation of the expected non-evaporable water content at each age based on the assumption that the fly ash acts only as an inert diluent.

Table 11.2-2 Non-evaporable Water Contents of Fly Ash Pastes and Expected Non-evaporable Water Contents Calculated on the Assumption that the Fly Ashes Act Only As Inert Diluents

Paste	1 day	3 days	7 days	28 days	90 days	180 days
LF1(25)	10.2	12.4	14.3	15.9	16.6	16.9
LF2(25)	10.7	12.9	13.8	16.3	16.8	17.7
LF3(25)	10.1	12.1	13.6	16.0	16.1	16.9
LC1(25)	11.2	14.0	16.2	18.2	18.7	19.2
LC2(25)	10.3	13.2	16.7	19.2	19.7	19.1
Expected For Inert Diluent	8.5	11.1	12.6	13.5	14.2	13.7

It is apparent from Table 11.2-2 that the non-evaporable water contents produced in the fly ash pastes are greater that calculated to occur in the absence of any fly ash chemical effect. This is true for both the low calcium and the high calcium fly ashes, and it is true from the first day on.

The most likely explanation, especially for the earlier effect, is that the hydration of the cement is in fact accelerated by the presence of the fly ash, of whatever type. Such acceleration has been found in various research reports.

At later ages, it would be possible to consider that some of the additional non-evaporable water comes into being as a result of the pozzolanic reaction, except that as previously discussed, the calcium hydroxide contents of these paste show little actual evidence of reduction in calcium hydroxide content that is the essence of the pzzolanic reaction.

The data of Table 11-2-2 also show that there is quite a distinction between the low calcium and the high calcium fly ashes with respect to the amount of "extra" non-evaporable water content found, especially after the first three days. The high calcium fly ashes generate substantially higher non-evaporable water contents. Presumably this means that there are indeed larger amounts of C-S-H gel being produced with high calcium fly ashes, by whatever mechanism.

11.3 SEM Studies of Long-Term Reaction

Scanning electron microscopy (SEM) examinations were carried out on portions of the same pastes used for mercury porosimetry and described previously in Section 10.1. These were pastes made from the reference cement L and from cement L and each of the fly ashes at the 25% replacement level. All of these were allowed to hydrate for approximately one year (actually between 363 and 377 days) before being sampled for the analyses.

For SEM examination the pastes were dried at 105 °C, fractured into prisms approximately 0.5 mm on a side, mounted on aluminum stubs with plastic cement, and coated with a gold palladium alloy using a sputter coater. The examinations were conducted with an ISI Super III-A SEM equipped with an EG and G Ortec energy-dispersive x-ray analysis (EDXA) unit.

11.3.1 Examination of Reference Cement Paste L

A number of SEM micrographs were secured for the 1-year old reference portland cement paste, to serve as background for interpretation of any changes induced by the presence of fly ash.

Figure 11.3-1 shows a typical area, in which a number of features of the microstructure of cement paste are visible. Fine textured C-S-H gel in small spheroidal clusters such as is shown at A is prominent feature, with a considerable amount of empty space in voids of the order of 5 μm (areas marked B) associated with them. Some C-S-H is in larger, more continuous deposits.

A somewhat more open area is shown in Figure 11.3-2. This zone apparently had a higher local water:cement ratio; as a result, there was more space to fill, and even after a year, much empty space remains. In such regions a fairly common feature is the occurrence of hollow shell hydration grains ("Hadley grains") such as the one shown at A. This is a shell which surrounded an individual cement grain; in the hydration process, the cement inside the shell dissolved, the dissolved material passed through the shell, and precipitated as C-S-H gel elsewhere in the system, leaving the empty shell.

Another new feature in the figure, around B, is the occurrence of long, thin ettringite needles. these are invariably associated with empty space, as can be seen in the figure.

Finally, the fine-structured basic C-S-H gel, which here is of the Type III variety, is locally prominent at C.

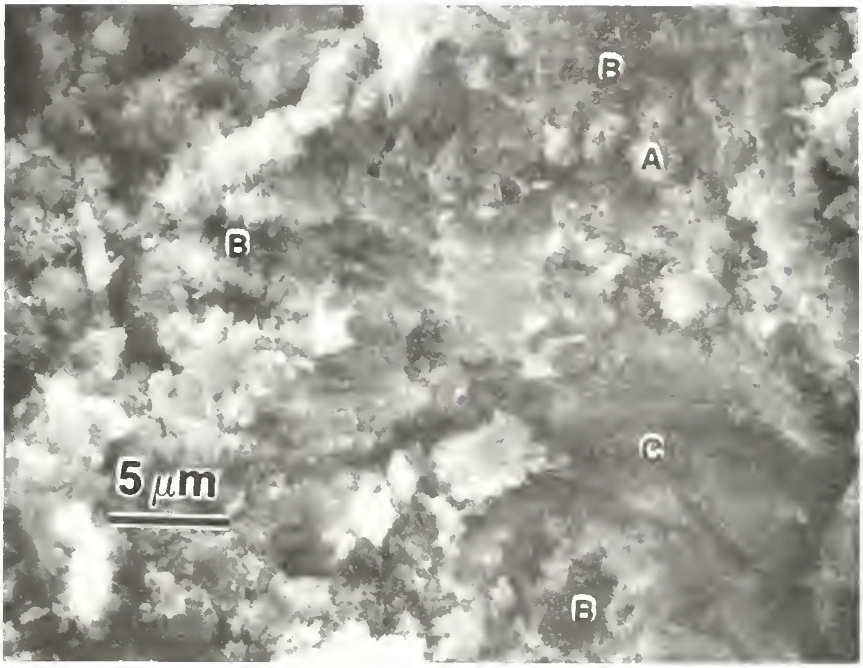

Figure 11.3-1 Scanning electron micrograph of reference portland cement paste L.

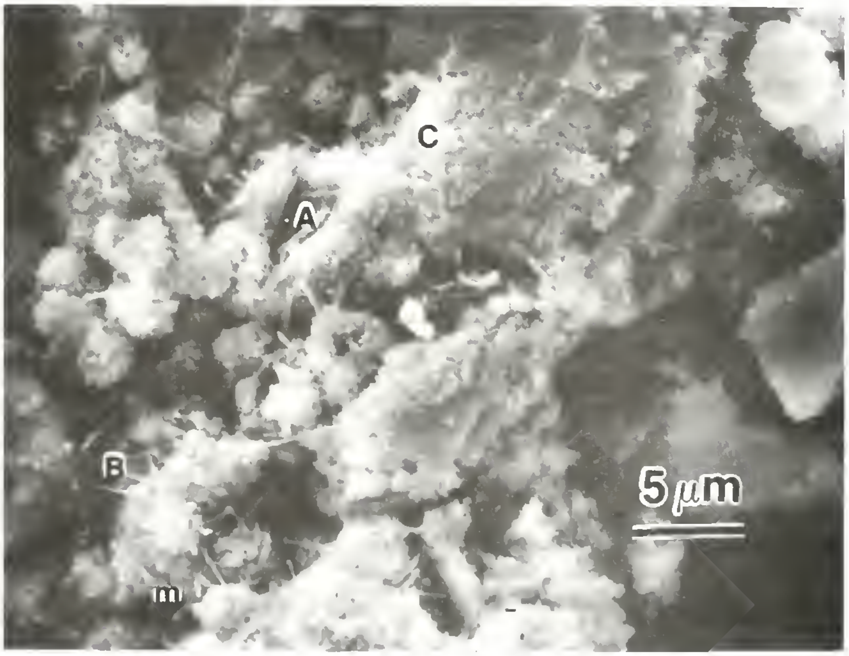

Figure 11.3-2 Scanning electron micrograph of reference portland cement paste L.

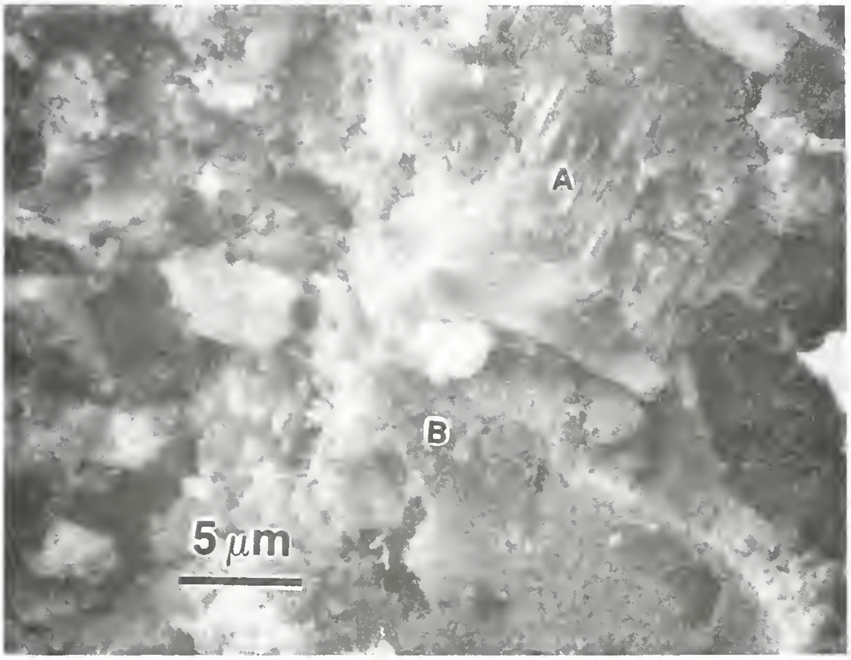

Figure 11.3-3 Scanning electron micrograph of reference portland cement paste L.

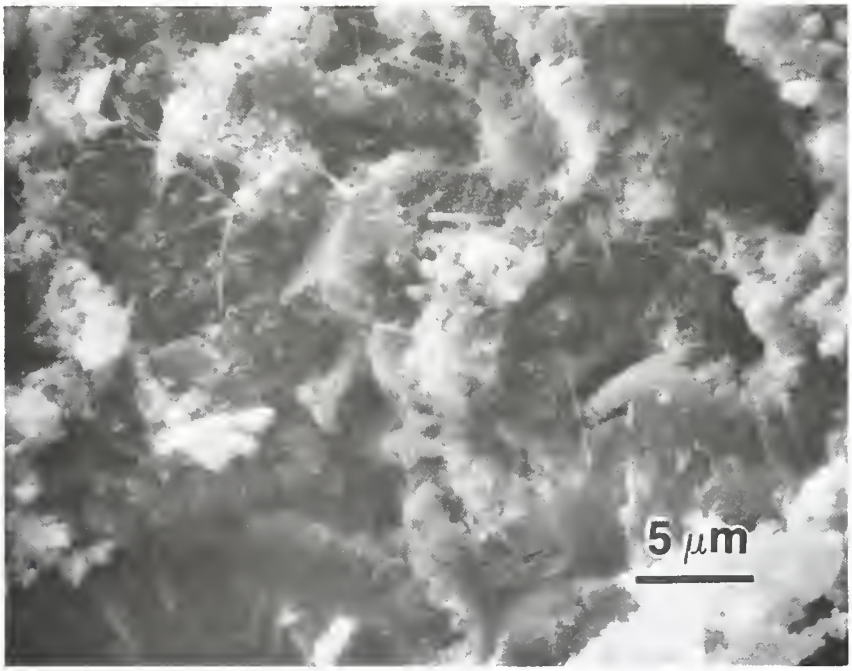

Figure 11.3-4 Scanning electron micrograph of reference portland cement paste L.

Another locally dense area of paste is shown in Figure 11.3-3. Here a fairly massive zone of calcium hydroxide occurs at A, and seems to be terminated by a layer of C-S-H gel at B. There is considerable void space to the left of the figure.

Finally, all of the features discussed previously are seen to be simultaneously present in Figure 11.3-4, which is also gives a quite representative impression of the overall "average" microstructure of this quite normal mature hardened cement paste.

11.3.2 Paste With Low Calcium Fly Ash F1

Figure 11.3-5 represents an area on the fracture surface of a sample of this paste. It is shown first to emphasize the point that fly ash spheres may be only loosely attached to the surrounding paste, and may not remain with the fracture surface being examined. The spherical holes marked A, B, and C are "sockets" remaining after the mechanical removal of residual fly ash spheres. The empty space is typically bounded by a 1 μm thick shell of dense materials, mostly calcium hydroxide. Also apparent in the micrograph are areas of layered calcium hydroxide (E), and of C-S-H gel (F), no different in appearance than corresponding zones in plain cement paste.

Figure 11.3-6 shows an approximately 15 μm fly ash grain that has remained attached to the fracture surface examined. The erosion caused by localized reaction at the surface is apparent. The degree of reaction is relatively small, in terms of the proportional volume of the fly ash that has been affected. There seems to be no distinct shell surrounding this sphere, regions of calcium hydroxide (A) and regions

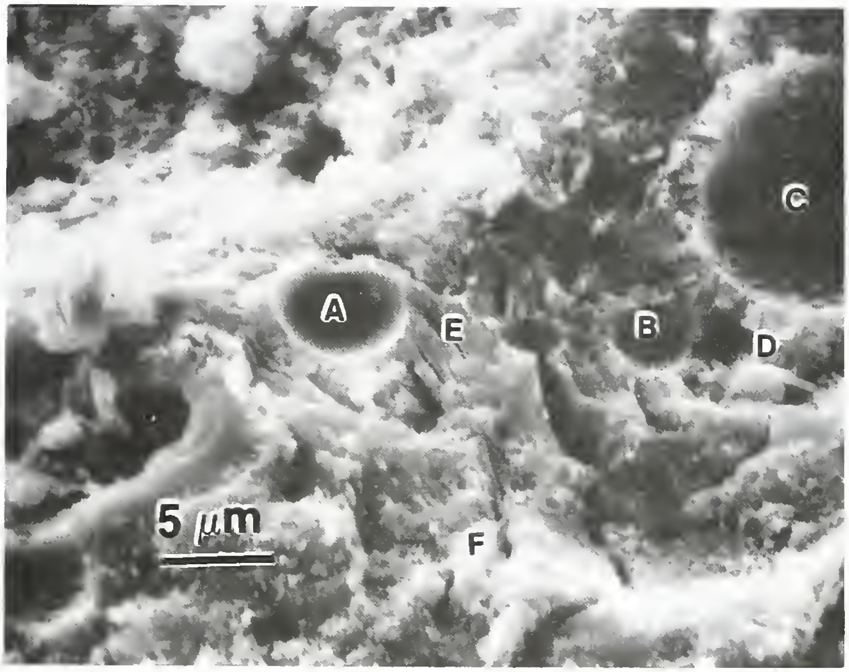

Figure 11.3-5 Scanning electron micrograph of cement paste with low calcium fly ash F1.

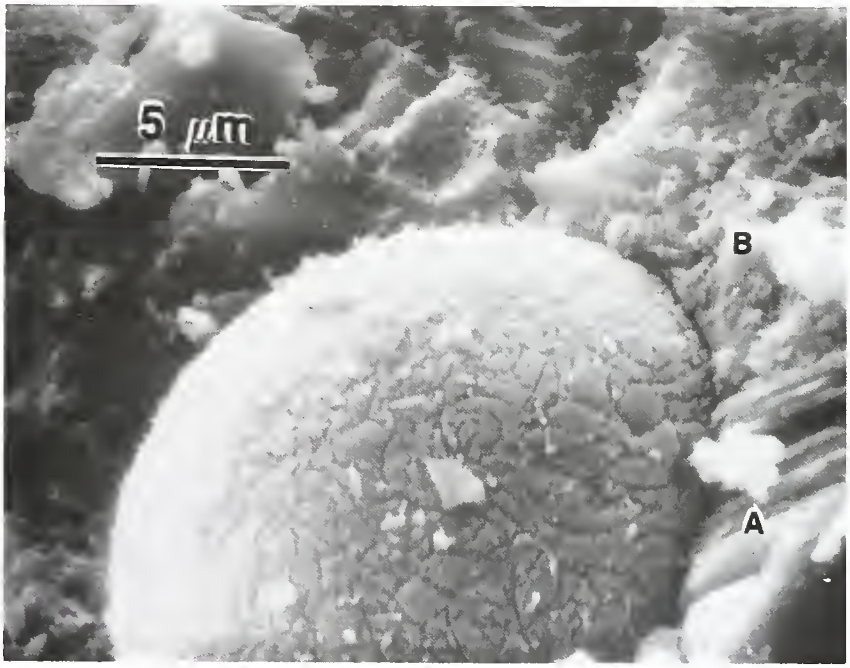

Figure 11.3-6 Scanning electron micrograph of cement paste with low calcium fly ash F1.

of C-S-H gel alternating around the periphery.

A similar morphology is evident in Figure 11.3-7. Here the fly ash is slightly more severely eroded at the surface, and the crystal outlines of the near-surface layer more definite. Most of the crystals whose outlines are exposed by erosion of the glass between them are blocky (A), but a few elongated laths (B), almost certainly of mullite, are loosely attached to the eroded surface.

A smaller fly ash grain (C), about 3 µm across, appears to be proportionately more reacted than the large sphere.

Figure 11.3-8 shows a very large fly ash grain, almost 80 µm across. Reaction here has been confined to a very thin layer, if indeed reaction has taken place at tall. The grain is cracked in the upper portion (A), but is not otherwise damaged. Such oversize grains will likely never react significantly in concrete, and might well be thought of as additions to the finest sand sizes present in concrete. A few small fly ash spheres (B, C) and some small empty sockets (D,E) are also present.

In general, it is evident that the fly ash spheres are occasional inclusions in the mass of hydrated cement material entirely similar to that produced in the reference paste, and that only a small percentage, by volume, of the usual fly ash sphere has been reacted and dissolved. There is a very large content of calcium hydroxide in the immediate vicinity of the residual fly ash spheres, but the so-called "pozzolanic reaction" is not very far advanced, even at 1 year.

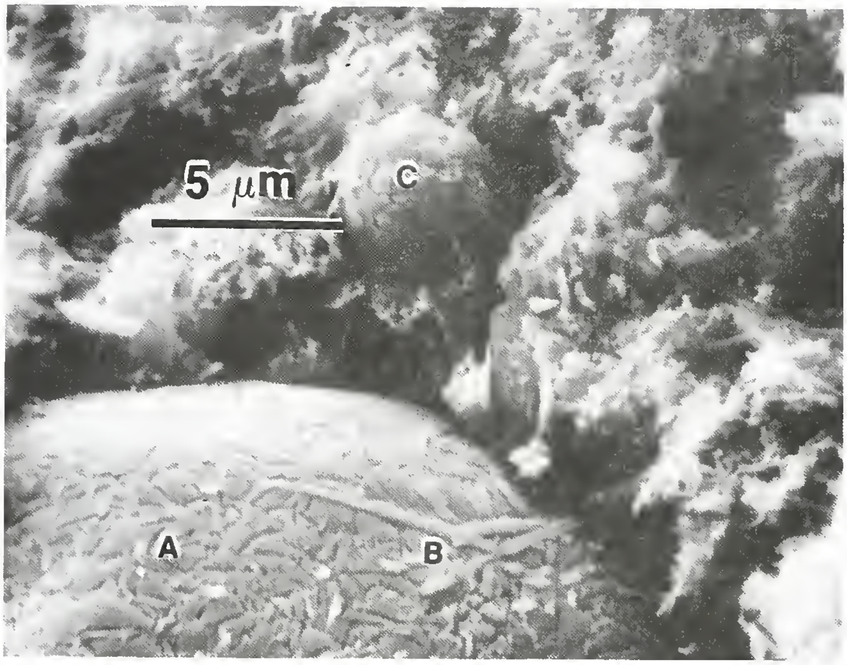

Figure 11.3-7 Scanning electron micrograph of cement paste with low calcium fly ash F1.

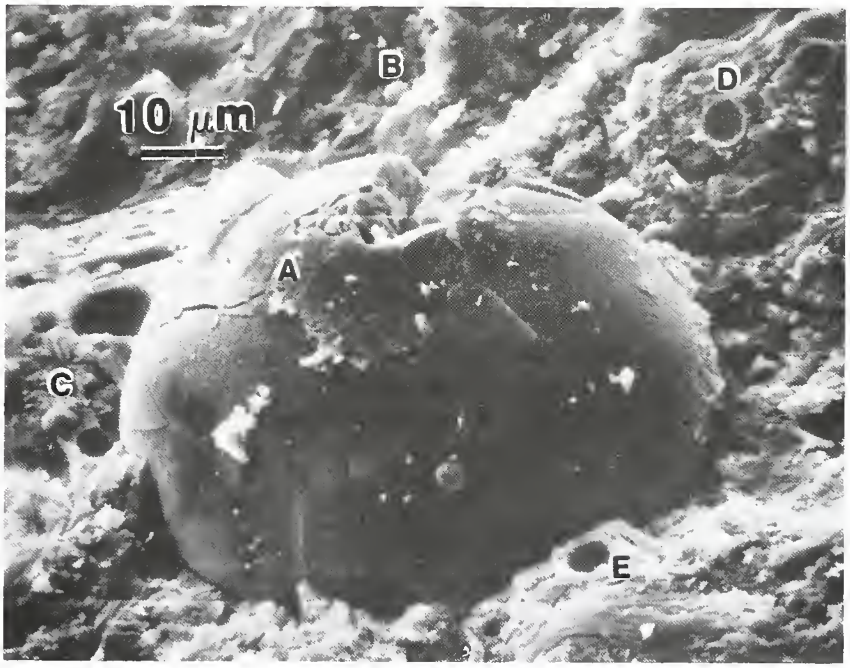

Figure 11.3-8 Scanning electron micrograph of cement paste with low calcium fly ash F1.

11.3.3 Paste With Low Calcium Fly Ash F2

The results obtained for this paste are similar in most respects to those for fly ash F1. Figure 11.3-9 shows an isolated 5 μm fly ash sphere almost entirely surrounded by calcium hydroxide (A), although a region of C-S-H gel (B) is nearby. The surface of the fly ash sphere is virtually free of any sign of reaction. Energy dispersive x-ray analysis (EDXA) of the sphere indicates that it has the normal composition, with silicon and aluminum being the main components, along with smaller amounts of calcium, potassium, and iron.

Fly ash spheres that show some definite signs of reaction are shown in Figure 11.3-10. The large sphere (A) shows definite indications of surface pitting, as does the slightly smaller sphere in the foreground (B). On the other hand, a very small sphere (above C) seems to have escaped even this limited amount of reaction.

The cracked oblate spheroid marked D that vaguely resembles a fly ash grain is most likely a residual portland cement particle undergoing hydration in situ.

In general we have found that recognizable fly ash grains are not uniformly distributed over the fracture surfaces of the paste specimens. Areas such as that shown in Figure 11.3-11 occur that show no fly ash at all. Here a central zone of calcium hydroxide crystals (A) is surrounded on the right by C-S-H gel (B) and on the left by an intimate mixture of gel and what seems to be fine monocalcium sulfoaluminate hydrate crystals (C).

On the other hand, some local areas, such as that shown in Figure 11.3-12, show many fly ash grains or their traces. Spheres A

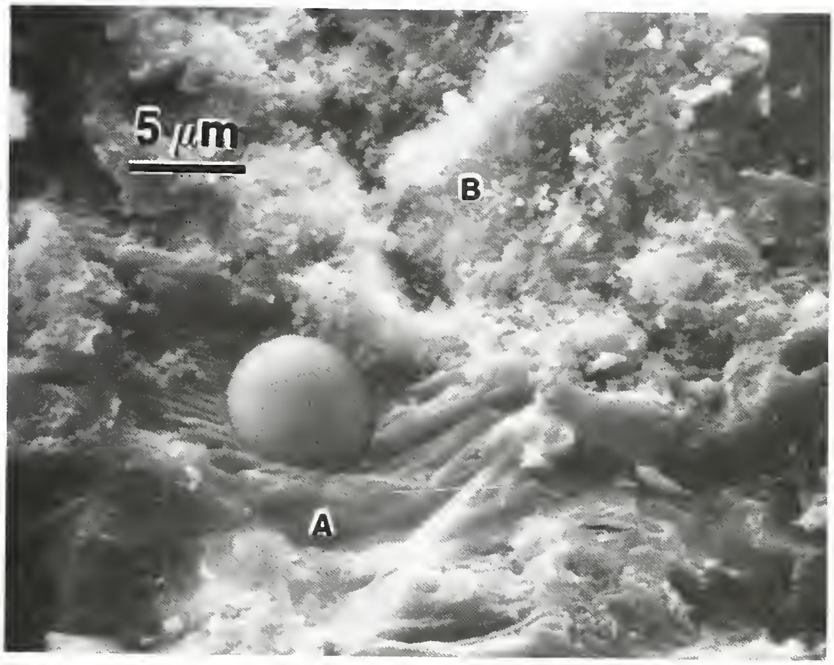

Figure 11.3-9 Scanning electron micrograph of cement paste with low calcium fly ash F2.

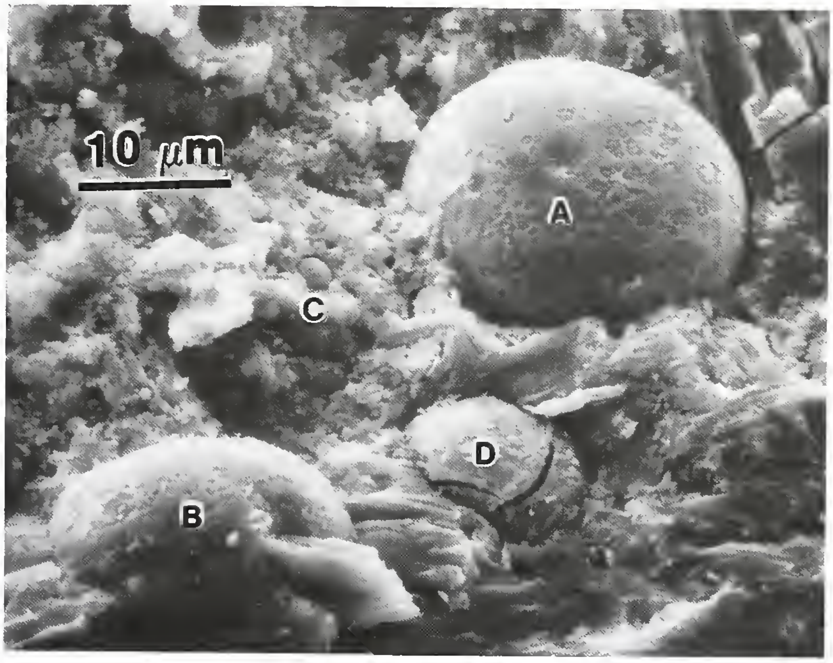

Figure 11.3-10 Scanning electron micrograph of cement paste with low calcium fly ash F2.

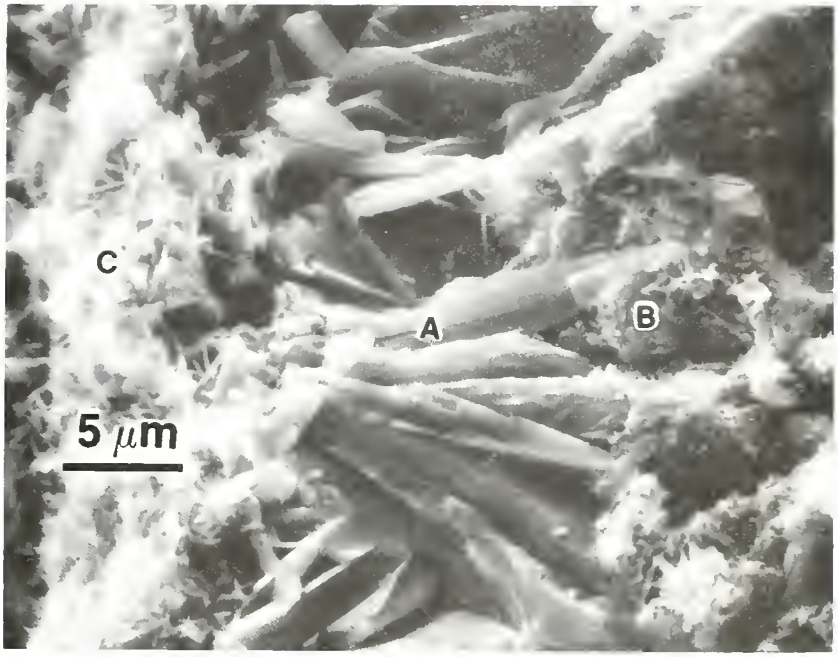

Figure 11.3-11 Scanning electron micrograph of cement paste with low calcium fly ash F2.

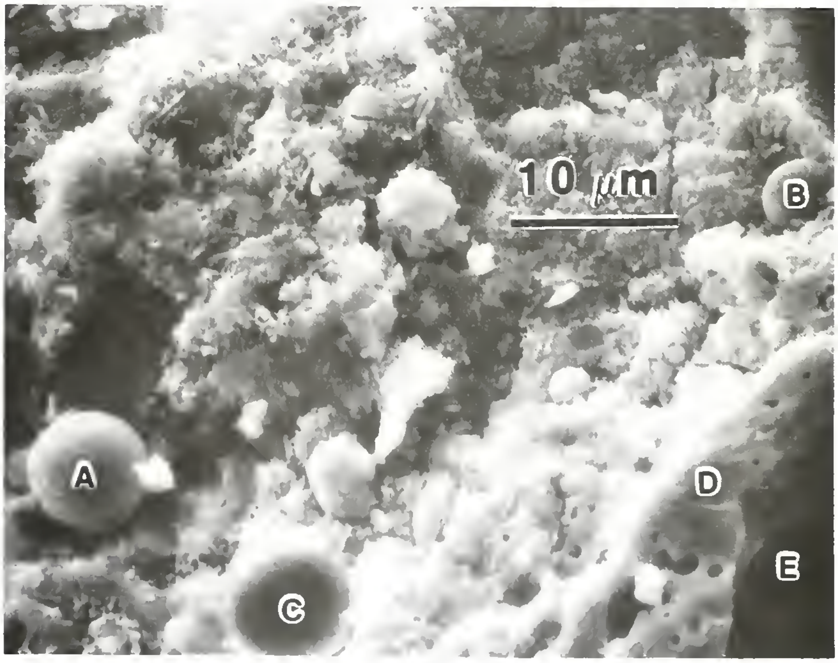

Figure 11.3-12 Scanning electron micrograph of cement paste with low calcium fly ash F2.

and B are small and clearly untouched fly ash grains, and a number of even smaller ones can be detected. An empty socket for a similar-sized detached sphere is apparent at C, and D is a relatively thick vesicular shell portion of a very large hollow fly ash grain, the interior of which (E) is empty. Somewhat atypically, there is no calcium hydroxide visible in this field, all of the hydrated cement surrounding the fly ash being C-S-H gel.

The extent of visible reaction that has taken place for the F2 fly ash in this paste seems, if anything, slightly less than the small extent of reaction detected in the paste with fly ash F1 discussed previously.

11.3.4 Paste With Low Calcium Fly Ash F3

This paste shows some evidence for a somewhat more advanced state of reaction than the previous one. Figure 11.3-13 shows most of an ~ 10 μm fly ash sphere (A) that is relatively deeply etched on the residual surface. More important, a gap of the order of 0.8 μm (B) seems to have opened up between the surrounding paste and the residual surface, presumably through reaction and dissolution of the outer layer of the fly ash. Sockets of two smaller fly ash grains are visible nearly (C, D). It is easy to see how residual spheres such as A can become detached and lost in the fracture process used to prepare the specimen surface for examination.

Rather more modest reaction, in the form of shallowly etched surfaces, are displayed on the two large fly ash spheres visible in Figure 11.3-14, and the single 15 μm sphere in Figure 11.3-15. No

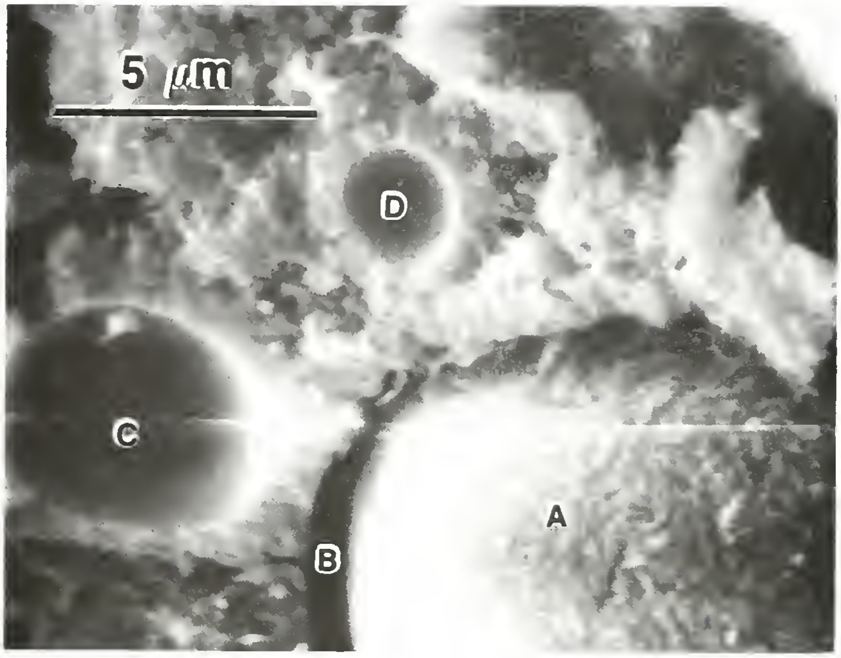

Figure 11.3-13 Scanning electron micrograph of cement paste with low calcium fly ash F3.

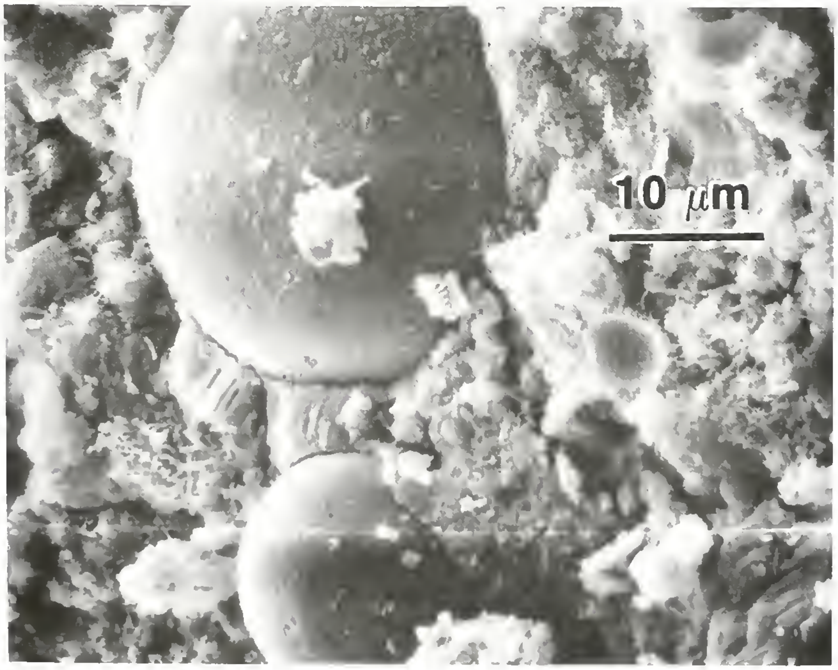

Figure 11.3-14 Scanning electron micrograph of cement paste with low calcium fly ash F3.

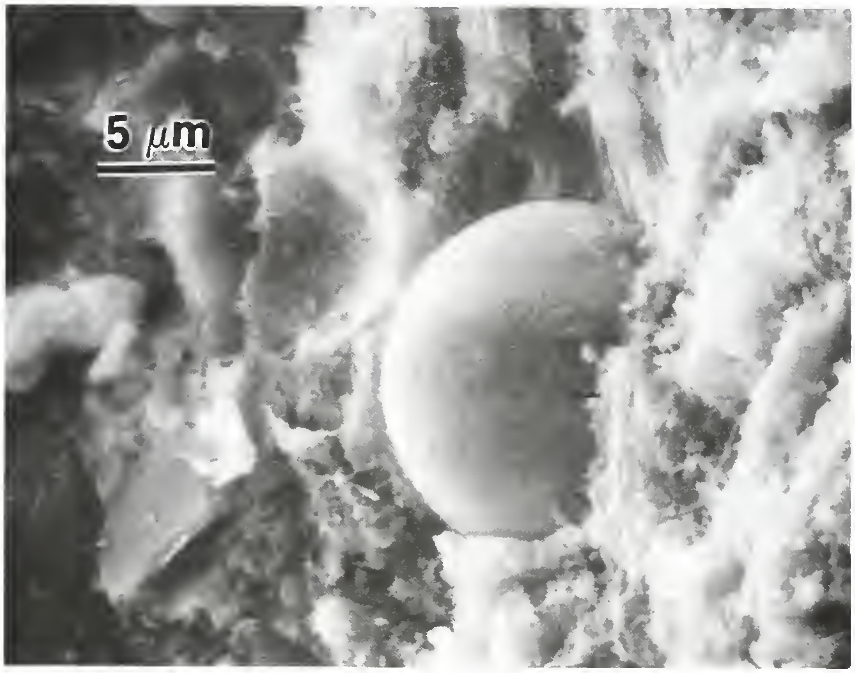

Figure 11.3-15 Scanning electron micrograph of cement paste with low calcium fly ash F3.

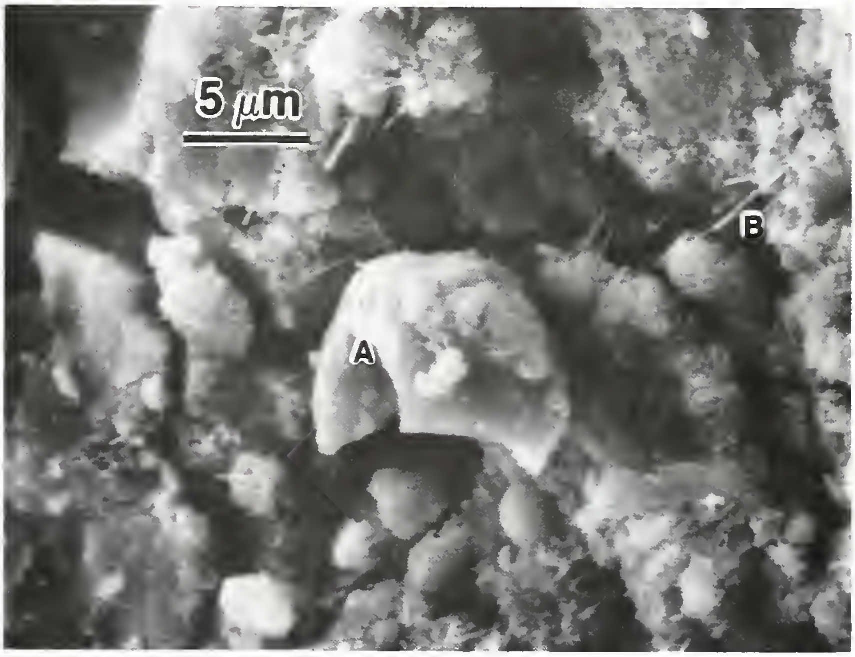

Figure 11.3-16 Scanning electron micrograph of cement paste with low calcium fly ash F3.

gaps surround these spheres, although should reaction have been allowed to proceed, gaps might have opened up subsequently.

Figure 11.3-16 illustrates the fact that even carefully prepared cement paste is not entirely homogeneous on a fine scale. This region of the paste is much more open, i.e. has much more visible intergrain ("capillary") porosity than the previous regions examined. The central feature (A) seems to be a shard comprising part of the shell of a hollow fly ash sphere. A few needle-shaped crystals of ettringite (B) occur projecting into the empty capillary space, but most of the hydration product is C-S-H gel.

In general then, examination of these "mature" low calcium fly ash bearing pastes indicate that while the cement hydration reactions are indeed in a mature state, the visible fly ash grains are only starting to become reacted, i.e. only the near surface zones have been visibly affected. This is not due to a local shortage of calcium hydroxide, since in many areas large deposits of calcium hydroxide are visible either in contact with the fly ash grains or in their immediate vicinities.

11.3.5 Paste With High Calcium Fly Ash C1

Examination of this paste disclosed only relatively minor differences from what was seen previously. For example, Figure 11.3-17 shows a 12 µm sphere that has had its surface eroded by reaction, more or less to the same degree as the low calcium fly ash spheres illustrated previously. The surrounding cement paste is also similar to what has been seen before.

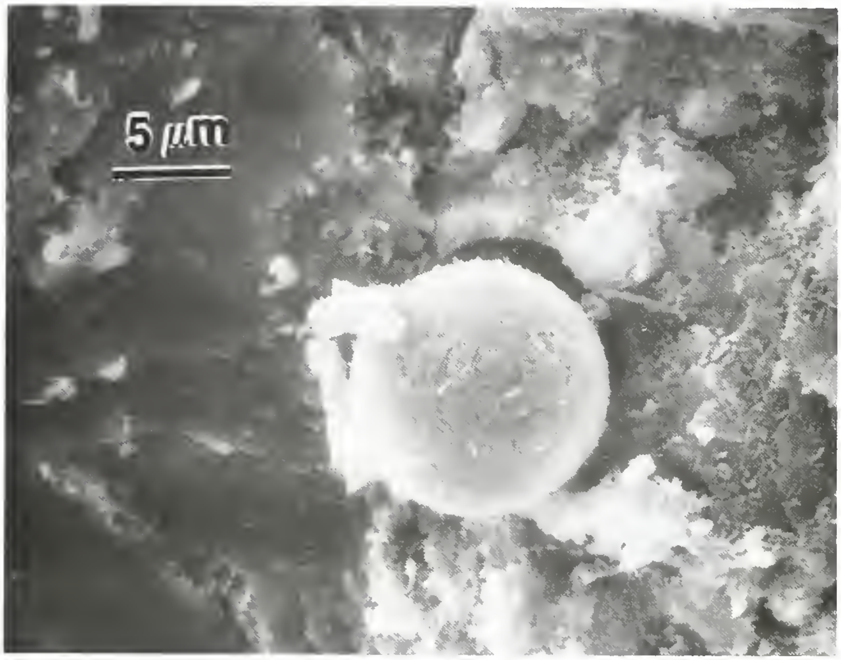

Figure 11.3-17 Scanning electron micrograph of cement paste with high calcium fly ash C1.

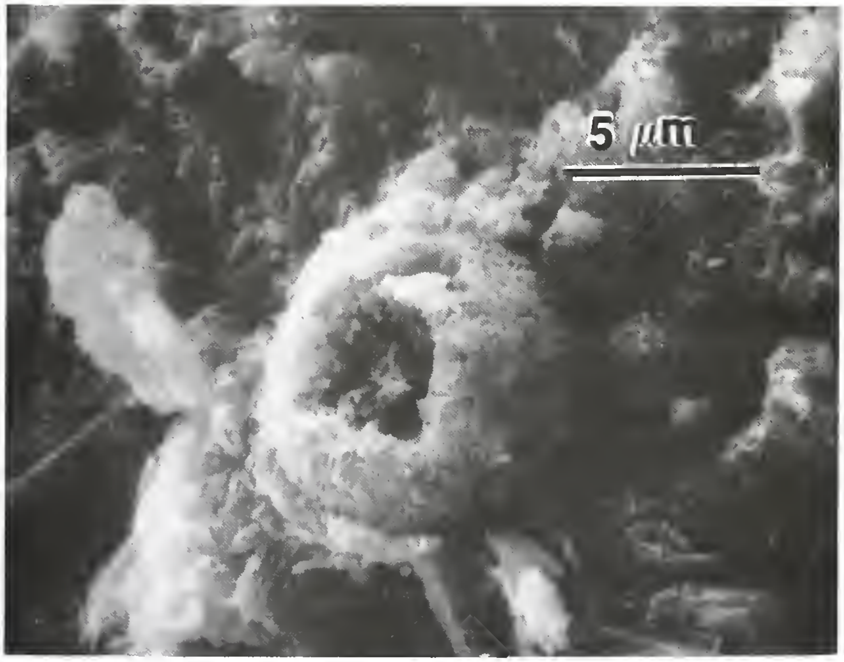

Figure 11.3-18 Scanning electron micrograph of cement paste with high calcium fly ash C1.

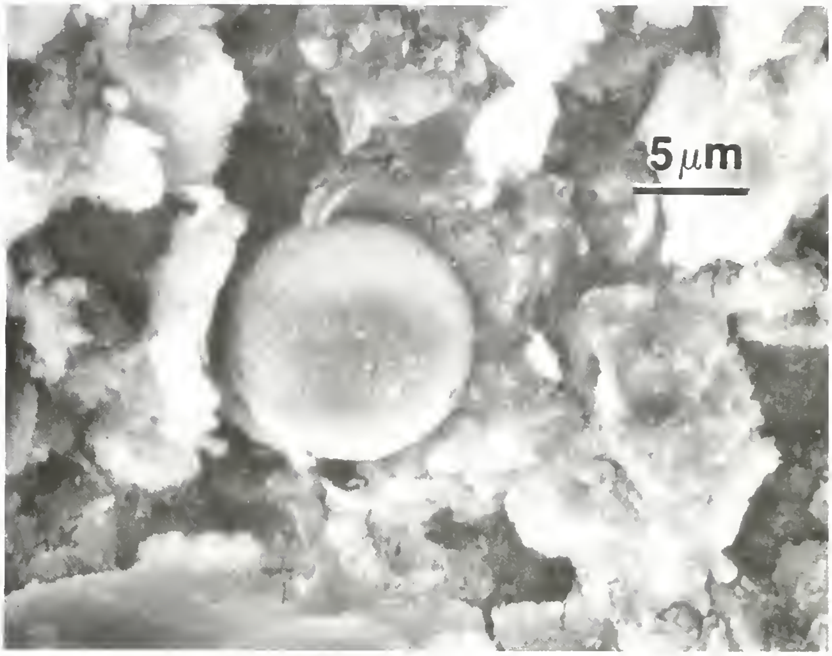

Figure 11.3-19 Scanning electron micrograph of cement paste with high calcium fly ash C1.

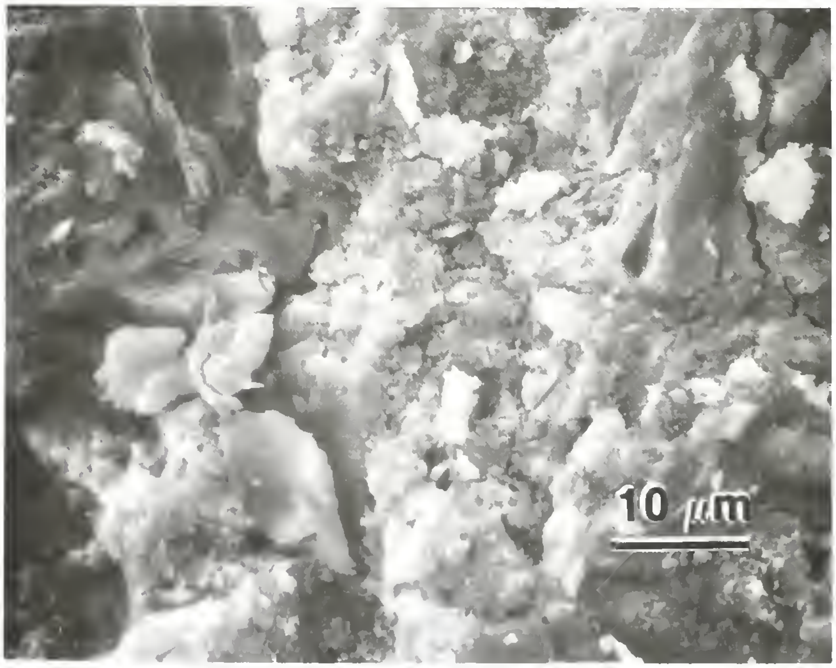

Figure 11.3-20 Scanning electron micrograph of cement paste with high calcium fly ash C1.

On the other hand, Figure 11.3-18 shows what appears to be a similar sized hollow sphere in a quite advanced stage of reaction. Very small thin plates seem to constitute a residual framework, with most of the glass removed from the thick shell.

Only a few grains like that shown in the preceding figure were observed; the majority resembled that of Figure 11.3-17, or that in Figure 11.3-19, where again the visible damage seems confined to the surface zone.

In this paste it was again noted that some local areas of fracture surface are entirely free of any visible fly ash spheres. An illustration is provided in Figure 11.3-20, which shows the usual C-S-H gel and calcium hydroxide zones.

In general, examination of this high calcium fly ash paste showed little that was different from the corresponding low calcium fly ash pastes previously discussed.

11.3.6 Paste With High Calcium Fly Ash C2

This fly ash gave some evidence of increased reactivity, although the fly ash grains again did not all appear to have reacted to the same degree. Fig. 11.3-21 shows a fly ash sphere that seems to have had much of its glass removed, although it is not evident to what depth the reaction has taken place. The grain is almost entirely surrounded by calcium hydroxide, so that the local availability of calcium hydroxide for the classical pozzolanic reaction is certainly high.

Figure 11.3-22 shows another sphere in a different area, but showing a similar state of visible reaction.

On the other hand, other fly ash grains are found in which seemingly much less reaction has taken place. Figure 11.3-23 shows a 12 μm sphere with an almost smooth surface and only a very narrow gap, if any, between its present surface and the surrounding paste. The paste surrounding the grain is mostly C-S-H gel; only a small part of the upper region of the periphery is in contact with calcium hydroxide (A). There is no indication that reaction is more advanced in this region than it is in the other part of the grain in contact with C-S-H gel.

In contrast to Figure 11.3-23, the fly ash grains in Figure 11.3-24 are in a field heavily dominated by calcium hydroxide. There seems to be no indication that the reaction has gone any faster because of this. The large vesicular grain marked A shows little sign of reaction, the surface being quite smooth. The two small spheres in the foreground (B and C) also seem hardly affected.

In general, visible signs of reaction in the particles of this fly ash are thus variable; some particles have clearly reacted to a significant degree, others have apparently remained untouched. It appears that the response has more to do with the make-up of a given sphere than with the local availability of calcium hydroxide deposits.

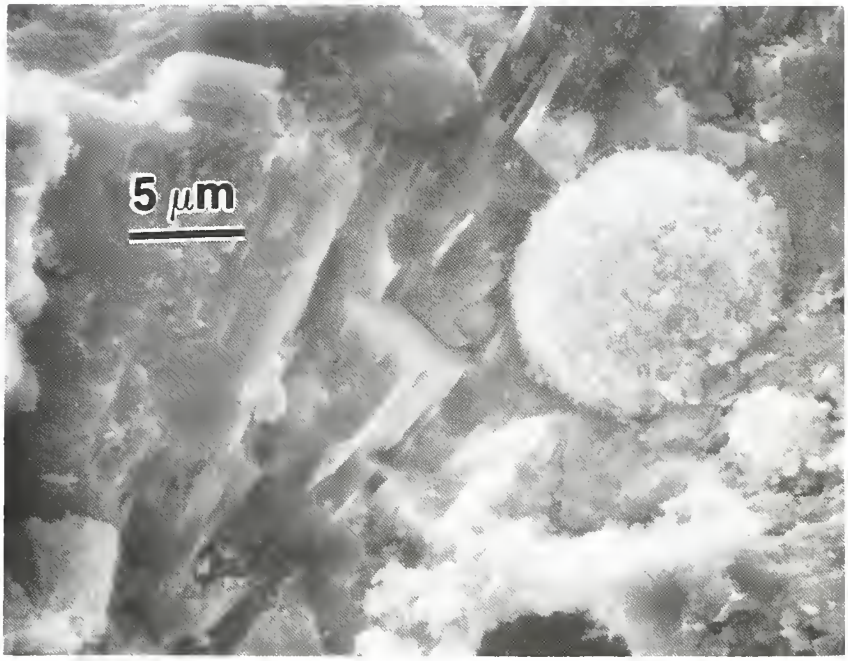

Figure 11.3-21 Scanning electron micrograph of cement paste with high calcium fly ash C2.

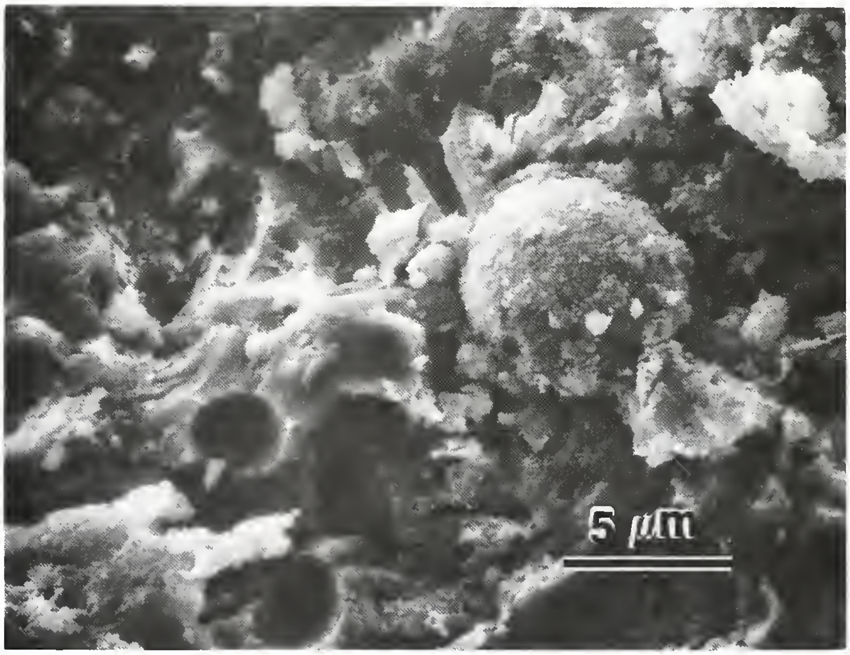

Figure 11.3-22 Scanning electron micrograph of cement paste with high calcium fly ash C2.

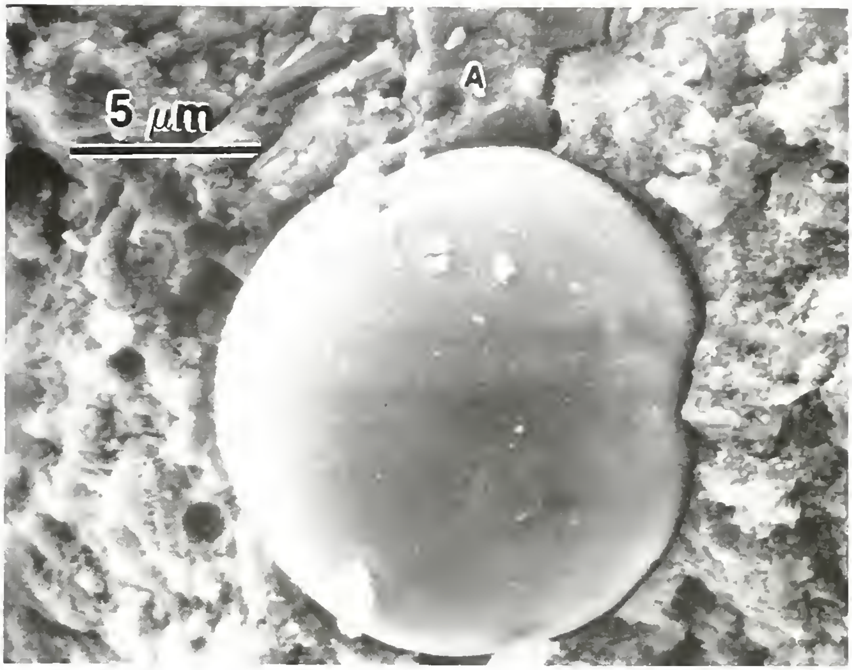

Figure 11.3-23 Scanning electron micrograph of cement paste with high calcium fly ash C2.

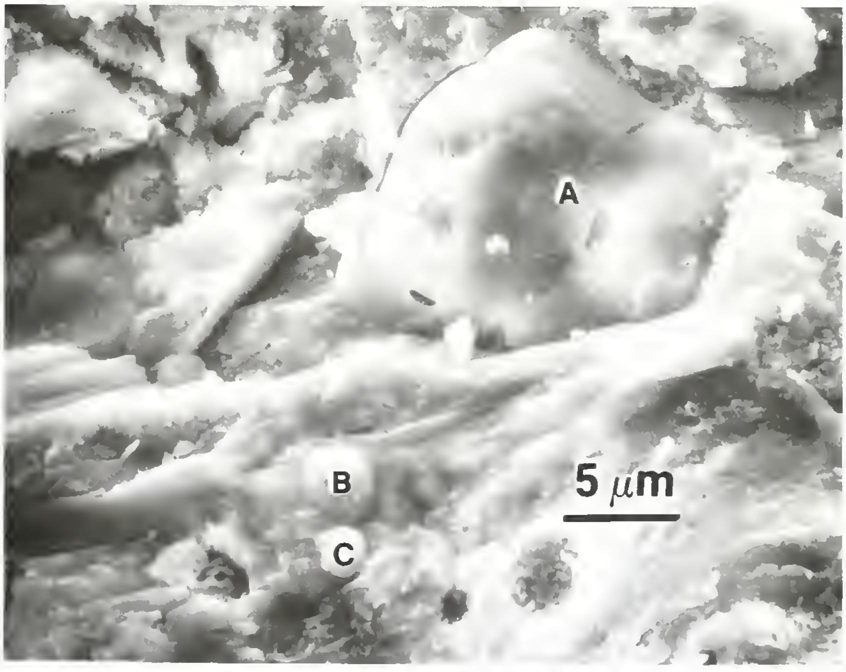

Figure 11.3-24 Scanning electron micrograph of cement paste with high calcium fly ash C2.

11.4 Leaching Studies Relating to the Nature and Reactivity of the Glass in Low Calcium Fly Ashes

A number of auxiliary studies were carried out in attempts to define the reaction potential of the glass present in low calcium fly ashes. It is well established that the glass in such ashes is the reactive component, the quartz, mullite, and iron oxide crystalline being considered largely inert in the cement environment.

These examinations were actually carried out as extensions of work begun on the predecessor project, used samples of fly ashes from the earlier sampling. The F1 fly ash in the present system is sampled from the same source as the NIP 1 fly ash of the earlier project; the F2 is from the same source as the IPL 1 fly ash of the earlier project, the F3 is from the same source as the PSI 2 fly ash of the earlier project, and the C1 fly ash is from the same source as the NIP 2 fly ash of the earlier project. A number of other fly ash sources had been sampled in the earlier project but were not included in the present project except for some limited extensions of earlier characterization work.

An attempt was made to develop a selective dissolution technique to preferentially dissolve (and hence measure) the glass in low calcium fly ashes by shaking in solutions of hydrofluoric acid (HF). It was found that this was not possible, since the HF solutions also dissolved the ferrite spinel (magnetite) components also present in the fly ashes and may have dissolved the finer hematite crystals and perhaps some of the less well crystallized mullite as well.

Thus the attempt to assess relative reactivity among fly ashes by chemical assessment of the glass content present did not succeed. However, chemical analyses of the material being dissolved from the fly ashes were useful in allowing an estimate of overall average glass composition to be made in some cases. The estimated composition average composition for the fly ash derived from the same source as the F1 ash used in this project was 70.1% SiO_2, 22.2% Al_2O_3, 2.7% CaO, 5.2% K_2O, and 0.1% Na_2O, on an iron-free basis. Analyses for two other low calcium fly ashes from the earlier project, coded PSI 1 and SIG 1, gave substantially similar results, as follows: 72.9% and 65.7% SiO_2 respectively; 19.0% and 26.8 Al_2O_3 respectively; 2.9% and 2.5% CaO respectively; 5.2% and 5.0% K_2O respectively, and 0.1% and 0.02% Na_2O, respectively.

At least to a first approximation these glass compositions can be looked on as being derived from local mixtures of two components of the inorganic part of the coal: quartz (which is composed of silica) and illite clay (which is composed of silica, alumina, potassium oxide, and minor contents of calcium and sodium oxides).

Studies were also carried out of the long-term chemical dissolution of several of these fly ashes in a mixture of potassium and sodium hydroxide, which constituted a simulated cement pore solution to some degree. The components dissolved from the fly ash by the alkali hydroxides were almost identical to those dissolved more rapidly by the hydrofluoric acid treatment, lending considerable confidence to the estimates of glass composition derived from the HF results.

A number of SEM micrographs were taken at various stages in the dissolution processes, and EDXA was used to estimate the local compositions of some of the fly ash areas. These led to two important generalizations concerning the low calcium fly ashes examined. The first is that the spheres are compositionally variable and respond to chemical attack in uneven fashion, some spheres being readily attacked, but other similar spheres (and even parts of spheres) being much more resistant. The second important generalization is that the potential for attack and dissolution of the glass by either HF or simulated cement pore solution is much greater than the degree of attack observed in the actual fly ash cement pastes described earlier, which had aged for one year. In general, for most spheres the glass can be completely stripped away, leaving behind only skeletal structures of mullite, some quartz crystals, and some iron oxide residue material, hanging together by tenuous contacts.

An idea of the degree to which glass reaction can occur to leave behind the non-reactive crystalline skeleton is conveyed in Figure 11.4-1, which shows two small spheres from the fly ash coded PSI 1, after exposure to 1% HF solution for 20 hours. Another example is shown in Figure 11.4-2, which shows the remains of a larger, partly hollow sphere from the fly ash taken from the same source as F3, exposed to the HF solution for 18 hours. In this figure are also included a number of smaller spheres, some of which have reacted to a much smaller extent. An example is the sphere marked A in the upper right corner.

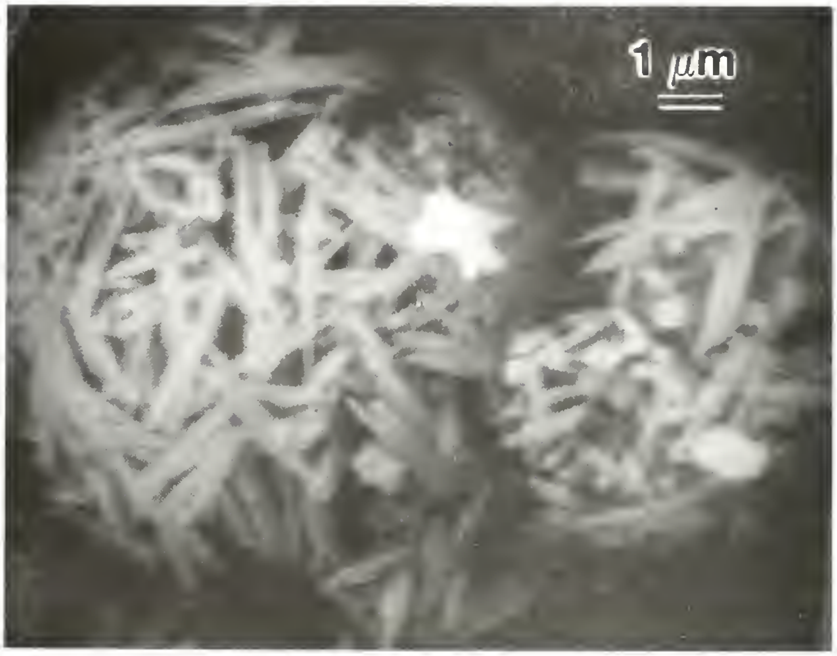

Figure 11.4-1 Scanning electron micrograph of fly ash IPL 1 after shaking for 20 hours in 1% HF solution.

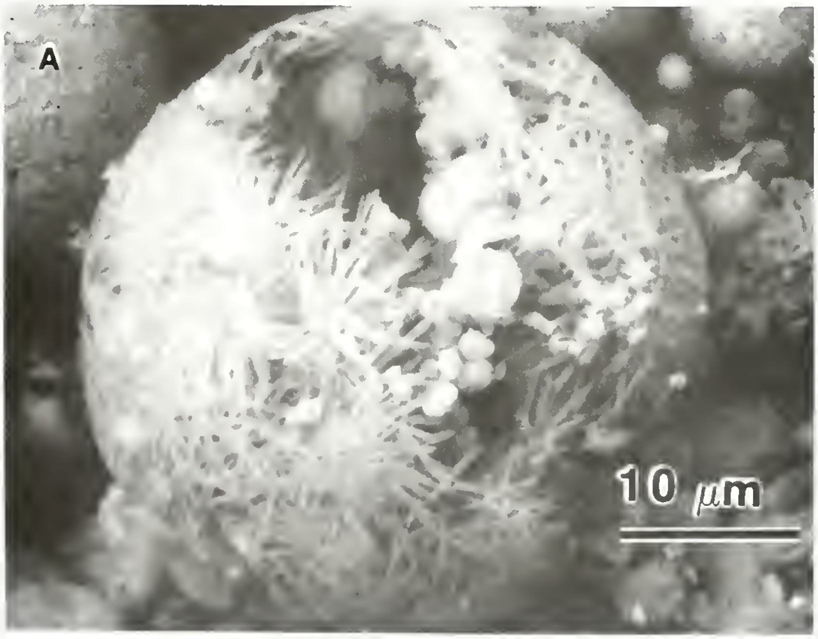

Figure 11.4-2 Scanning electron micrograph of fly ash PSI 2 after shaking for 18 hours in 1% HF solution.

12.0 SUMMARY AND CONCLUSIONS

The considerable body of experimental work carried out in the course of this project is difficult to summarize in a concise manner. The variety of materials and experimental procedures used and the many findings developed do not lend themselves to easy generalization.

In this Chapter, we have chosen first to restate the original objectives of the project, then to summarize the detailed experiment findings as carefully as possible, and finally, to present a set of formal conclusions stemming from the work.

12.1 Restatement of Project Objectives

The following information is derived from the original research proposal submitted to FHWA and IDOH, some of it being condensed and paraphrased.

Previous to carrying out of the predecessor project, information on Indiana fly ashes was sparse and scattered. The predecessor project, which entailed a thorough study of the nature and properties of 14 representative Indiana fly ashes, provided a good picture of the characteristics to be expected of the fly ashes produced from various sources around the state.

The fundamental thinking behind the present (Phase II) project was "to carry the investigation to the next required stage, that is, the investigation of the actual effects produced by different fly ashes in concrete, specifically in practical concrete of the type specified for highway pavements and structures."

The formal objectives were as follows:

"The primary objective ... is that of studying the details of the performance and behavior of concrete produced with fly ashes representative of those that may be used in highway concrete in Indiana."

"A secondary objective is .... to develop the maximum of objective scientific information concerning the behavior and influences of fly ashes in general, when incorporated in concrete."

"The final objective is to report the findings and results in such a way as to provide the maximum possible utility, first to IDOH materials and construction engineers who will be involved in specifying and supervising the placement of fly ash concrete in highways and associated structures, and then to the technical community at large."

We hope that the work done and the report provided completely fulfill these objectives.

12.2 Summary

Because of the extensive body of material to be summarized, we have broken this Section into a number of separate areas.

12.2.1 Preliminary Stages

After a thorough review of the technical literature on the mix design of fly ash concretes, it was decided that existing mix design methods for fly ash concrete would probably not be adequate to guarantee performance of field highway concrete in the face of expected major variations in fly ash quality and properties from job to job, and even within large jobs. In particular, no existing method concerned itself with the important areas of concrete durability.

Accordingly, we developed a new method to meet this need, the so-called "Constant Paste Quality" (CPQ) method, the details of which has been thoroughly and carefully presented in this report. Parenthetically, the method has been presented at a symposium on fly ash mix design held by the American Concrete Institute, and the paper describing it has been approved for publication.

The method has been used to design all of the concrete produced in this project.

Selection of materials for this investigation was carried out with the advice and assistance of IDOH. A representative suite of five fly ashes (three of the low calcium type and two of the high calcium type) was assembled, two different representative cements widely used in Indiana were chosen, and representative coarse and fine aggregate materials selected. Preliminary investigations were carried out on the effectiveness of air entrainment when fly ash is used at several replacement levels. It was found that by use of the foam index method, it was possible to predict the specific demand of each mix for air entraining agent, so that all batches could be prepared with air contents required to insure freezing and thawing durability.

As part of the preliminary studies on mix design, a limited analysis of the economic effect of using fly ash in highway concrete was carried out. It was concluded that with the CPQ mix design procedure, the increased volume proportion of aggregates that could be used did lead to some economic advantage, but the main cost savings in using fly ash still derives from the lower cost of the fly ash as compared to the cement it replaces.

12.2.2 Effects of Fly Ashes on Fresh Concrete Properties

It was found that the mix design method, properly applied, provides for very consistent control of the slump and air content of fresh concrete, regardless of the specific fly ash used and the level of cement replacement. In addition, the method was found to provide for very close control of concrete unit weight, regardless of difference in fly ash density.

The fly ash concretes were found to show qualitative improvements in ease of placing and finishing over the reference plain concretes batched at the same slump. These indications were confirmed in the reduced VeBe times found for the fly ash concretes.

The use of the foam index test was confirmed as a method for predicting the necessary dosage of air entraining agent to arrive at a consistent air content, and the relationship between foam index and needed dosage was shown to be satisfactorily linear.

It was found that all of the fly ash concretes are retarded with respect to set. The extent of retardation varied from minimal to as much as 5-1/2 hours, and depended on the specific cement used, as well as the specific fly ash and the replacement level. One particular high calcium fly ash gave consistently higher set retardations than any of the others, and probably would necessitate use of an accelerating agent when used in practice.

12.2.3 Influence of Fly Ash on Properties Measured With Fresh Cement Pastes

It was found that fly ashes affected a number of properties of fresh cement pastes. The pastes studied were batched to simulate the paste in the specific concretes studied in all respects except that no aggregate component was included.

It was found that only small effects were measured for the "spread" of the various pastes as determined using the minislump cone. Thus the pastes in the reference and fly ash concretes of equal slump themselves behaved rheologically similar to each other. However, it was noted that this similarity, i.e. the lack of effect of the fly ash on paste rheology, was likely due to the static nature of the minislump cone test. It was observed that much more significances would likely have been noted under some standard degree of impact or vibration, such as is used in the Vebe or flow tests.

The set retardations associated with fly ash in cement paste were studied and found to be generally similar to those produced by the same fly ash in concrete.

The effects of the fly ashes on the early hydration processes as indicated by heat production were studied by monitoring temperature evolution of pastes in a standard quasi-adiabatic environment. All of the fly ashes delayed the temperature build up associated with early cement hydration, and all reduced the maximum temperature achieved, but there were significant differences among the different fly ashes in this regard. Pastes batched with the high calcium fly ashes achieved significantly higher maximum temperatures than those with the low calcium fly ashes, although the times to achieve these maxima were extended.

All of the fly ashes were found to increased the dormant period in cement hydration to some degree. It was found that the specific fly ash that gave high set retardation across the board also increased the duration of the dormant period to a greater extent than the others.

It was possible to correlate the initial and final set times of the various pastes with the corresponding time-temperature curves, and it was found that initial set takes place significantly higher up on the temperature peak with fly ash pastes than with the reference paste.

12.2.4 Effects of Fly Ashes on the Mechanical Properties of the Hardened Concrete

A considerable body of information has been acquired on the effects of fly ash on the mechanical properties of hardened concrete.

Elastic Properties

Measurements of longitudinal and transverse strain were linearly related to static applied stress with very high degrees of precision, and accurate measurements of static modulus of elasticity and Poisson's ratio were made.

The Young's moduli recorded for the fly ash concretes ranged between 3.2 and 5.6 million psi, well within the normal concrete range. Young's modulus was found to be a precise and linear function of the compressive strength of the concrete concerned. These test concretes ranged in age from 2 days to 6 months, and in compressive strength from less than 2400 psi to as much as 6300 psi.

Measured values of Poisson's ratio ranged between 0.17 and more than 0.23, and like the Young's modulus, were found to be closely and linearly related to compressive strength. These relationships may hold generally for fly ash concretes. If they do, they can provide easy estimates of elastic parameters at various stages of concrete development from a knowledge of the strength gain curve for a particular mix.

The dynamic modulus of elasticity was measured on the entire suite of fly ash concretes at ages ranging from 1 day to 6 months, using the pulse velocity method. The values found were significantly higher than the static moduli for similar concretes. This is to be expected in view of the fact that the dynamic measurements are done in the wet state, and are done so rapidly that no creep component can affect the measurement. It was found that the dynamic modulus as a function of age for the plain reference concretes varied depending on the specific cement used, but that when fly ash was incorporated, these cement-specific effects largely disappeared. However, strong differences in the dynamic modulus vs. age relationship were detected between similar concretes batched with different fly ashes.

It was found that the dynamic elastic modulus for the fly ash concretes, while initially lower than those of the plain reference concretes, could match or exceed these values after 28 days.

Compressive and Flexural Strengths

It was found that concretes batched with the fly ashes attained generally similar compressive strengths to reference plain cement concretes at each age. A relatively narrow band of strengths was observed for the different fly ashes at the lower replacement level, but this band was found to broaden at the 25% replacement level, where differences among the fly ashes became more prominent. At this higher level the compressive strengths for the first 3 days did not quite match the reference concretes, and even at 28 days there was a slight reduction observed for two of the less reactive low calcium fly ashes.

On the other hand, in many cases it was found that by 90 days the fly ash concretes achieved compressive strengths substantially higher than those of the reference plain cement concretes.

It was found that the effects of the fly ashes on the development of flexural strengths were somewhat different from those described above. Incorporation of fly ash concretes were usually found to have lower flexural strengths than the reference concrete at any given age, but especially at 7 and 28 days. The high calcium fly ashes did somewhat better in this regard than the low calcium ashes.

These differences in effect between compressive strength and flexural strength measurements may imply that the usual relationship found between the two for plain concretes does not necessarily extend to fly ash concretes, a point of some concern for designers.

It was found that for plain cement concrete, the specific cement used had a significant influence on flexural strength development, but this influence was lost when fly ash was incorporated. This behavior for flexural strength parallels similar behavior for dynamic modulus described earlier in this Chapter.

The actual values of flexural strength vs. time for the different fly ash concretes were found to be within a relatively narrow band, virtually independent of the cement used. For long hydration periods (90 days or longer) the general level of flexural strength does approach the level reached by the plain concretes, although it rarely exceeds it. Generally speaking, flexural strengths at the 25% fly ash replacement level are slightly less than those at the 15% replacement level.

Density

With few exceptions, it was found that the measured densities of all concretes increased with time, with an overall relative increase of about 8% observed between 1 day and 180 days, independently of whether fly ash is used or not. This is interpreted as indicating a progressive densification of the internal structure of all of the concretes as hydration proceeds.

12.2.5 Effects of Fly Ash on Durability-Related Properties

A considerable portion of this research was aimed at documenting the effects of the fly ashes on measured values of durability related properties. Some of the parameters were measured directly on concrete; others required the preparation of cement pastes, which were batched in identical proportions from identical components, but without sand and coarse aggregate.

The results in all cases were favorable to the use of fly ash. It was found that a finer pore size distribution is developed; that the chloride permeability is significantly reduced; that freezing and thawing resistance is maintained; that the pore solutions become less alkaline, reducing the risks of alkali aggregate reaction, and that the capability of the concrete to immobilize chloride added in the mixer is significantly enhanced, i.e. that protection against chloride-induced corrosion may be improved. The only partly unfavorable effect found is that the reduction of pore solution alkalinity, useful in protecting against alkali-aggregate reactions, may slightly reduce the reserve alkalinity with respect to corrosion potential. This is not considered to be a serious effect.

The specific findings developed are detailed below.

Mercury Porosimetry

The pore structure of mature fly ash pastes and of a reference cement paste, all hydrated for one year, were examined by mercury porosimetry.

The results were quite similar for all of the low calcium fly ash pastes. Their pore structures a somewhat finer mean pore diameter than the reference paste, and a slightly higher total pore volume. The extra pore volume occurs in the finest size classes, i.e. of the order of 100 A or less in diameter. Such extremely fine ("gel") pores are unlikely to be involved in permeability, and likely represent extra internal pores of additional cement hydration product formed in these systems.

The pastes with high calcium fly ashes show somewhat different pore structures. For one of them the pore structure is significantly finer than for the other pastes (mean pore diameter approximately 200 A), but for some reason there is no extra pore volume in the finest sizes. For the other, the pore structure is also finer than the reference cement paste, but the shape of the distribution curve is different from that of the C1 paste.

All of the fly ash pastes show pore structures finer than that of the reference paste, suggesting that the fly ashes confer at least some degree of additional impermeability to the system. Their use would thus tend to render the concrete more resistant to durability problems.

Chloride Permeability

Chloride permeability measurements were carried out on concrete specimens aged 6 months before the test. It was found that each of the fly ashes reduced the measured chloride permeability significantly. The low calcium fly ashes were more effective in this regard than the high calcium ones, with one of the three being particularly effective. The degree of reduction was greater at the higher fly ash replacement level in all cases. The reference plain concretes had "low" chloride permeabilities; all of the fly ash concretes except one fell into the "very low" category.

The improvement in resistance to chloride penetration was found not to follow the same order as improvement in concrete strength.

In general, the reductions in chloride permeabilities were deemed to be significant enough that real benefit could be expected with respect to rate of chloride penetration into fly ash concrete as compared to plain concrete of the same general class.

Freezing and Thawing Resistance

All of the fly ash concretes, as well as the reference concretes, performed very satisfactorily in the freezing and thawing tests, giving durability factors at 300 cycles of the order of 75 to 80%, and showing no evidence of physical distress or weight change on the test bars. It should be recalled that the dosage of air entraining agent used in each batch was adjusted on the basis of prior testing so as to produce a 6% air content. Thus, it is evident that if a proper air void system is generated in fly ash concrete, no difficulties with freezing and thawing should be expected.

Pore Solution Parameters

Studies of the effects of the different fly ashes on the chemical composition of pore solutions pressed from mature (7-month old) pastes indicate that there is a reduction of the order of 30% in the OH^- ion concentration for the low calcium ashes, but a rather lesser reduction for the high calcium ones. The reduction in alkalinity is primarily due to reaction with K^+ ions; Na^+ ions are not significantly removed, and for the high calcium fly ashes, seem to be liberated by the reaction, partly counterbalancing the effect of K^+ ion removal.

The general reduction in alkalinity is a very favorable effect with respect to possible durability problems of alkali aggregate reaction, although there may be a slight negative connotation with respect to steel corrosion protection.

Effects on Pore Solution Chloride Levels

Pastes in which chloride was deliberately incorporated at the level of a 1% $CaCl_2$ treatment were examined after 3 months. In the reference paste the concentration of dissolved chloride had been reduced to about 1/4 of its original value by reaction with cement. Significant further reductions were found to occur with fly ash incorporation, especially with the high calcium fly ashes, where the residual chloride concentration dropped to about 10% of the original value.

These results indicate that fly ash use results in a concrete that "fixes" most of the dissolved chloride, i.e. renders it ineffective in terms of causing steel corrosion, to a greater degree than plain concrete does. Thus the likelihood of steel corrosion triggered by the presence of chloride is reduced. This would also probably provide benefit in the situation where chloride is penetrating from the outside rather than being incorporated as an admixture. The former is the common case with salt-induced steel corrosion in bridge decks.

12.2.6 Studies of Fly Ash Reactivity

A number of studies on the reactivity and details of the reactions of these fly ashes have led to some surprising findings. In general terms, it appears that the degree of pozzolanic reactivity exhibited by these materials, at least during the first year of hydration, is much less than has been anticipated. The specifics of the results are summarized below.

Pozzolanic Reaction as Measured by Residual Calcium Hydroxide

Determinations of the actual calcium hydroxide content of pastes with each of the fly ashes were carried out for ages up to 1 year. The results showed quite dramatically that the calcium hydroxide content found in almost all cases was approximately that predicted for the same cement, diluted with a chemically inert material in the same proportion as it was with fly ash. This surprising results was found to be true for all of the low calcium fly ashes and for one of the two high calcium ashes. With the other high calcium ash, somewhat more calcium hydroxide than expected on this basis was found over the first few weeks, but apparently this excess declined (by pozzolanic reaction?) to the general level of that found with the other fly ashes.

Non-Evaporable Water Content

The non-evaporable water content in the fly ash pastes was significantly higher than that predicted for the same cement diluted with a chemically inert material in the same proportion as the fly ash used. This was true for both low calcium and high calcium fly ashes, although more strongly pronounced for the latter. Some "excess" non-evaporable water content was detected as early as 1 day, but the effect became pronounced after three days. The interpretation made is that the presence of the fly ash likely stimulated additional cement hydration, and resulted in more nearly complete cement reaction at any given age.

SEM Studies

Scanning electron microscopy (SEM) studies indicated that for the low calcium fly ashes, even at 1 year, there was only very small visual evidence of fly ash reaction, taking the form of light etching around the surfaces of the fly ash spheres. The presence of large amounts of calcium hydroxide near, and in some cases completely surrounding, the fly ash grains was evidence that failure to react more extensively was not due to any local shortage of calcium hydroxide. It was found that some of the grains in the high calcium fly ashes showed more visible evidences of having reacted during the year's exposure, but even for these fly ashes most of the spheres were only modestly etched.

Chemical Leaching Studies

Studies of the comparative resistance to leaching of fly ashes by hydrofluoric acid (HF) and by strong alkali hydroxide solutions were carried out for some low calcium fly ashes. An estimate of the chemical composition of the fly ash glass was arrived at from these studies. The potential extent of chemical dissolution of fly ash glass was pictured, and it by comparison with these pictures visually illustrating complete dissolution of the fly ash glass, it is confirmed that the fly ashes in the cement pastes previously discussed have reacted only to a very small degree.

12.3 Conclusions

1. A new method of fly ash concrete mix proportioning, (the "Constant Paste Quality" method) has been developed, evaluated, and used to design all of the concrete for specimens used in this project. The method has been presented at an American Concrete Institute symposium and has been accepted for publication by ACI.

2. In using the CPQ mix proportioning procedure, for fly ashes of favorable physical characteristics the volume percentage of aggregate used in a given concrete can be increased significantly. However, a brief economic analysis indicates that the main cost savings would still derive mostly from the lower cost of the fly ash compared

to that of the cement it replaces.

3. The CPQ mix design method intrinsically detects and takes advantage of the water-reducing abilities of some fly ashes, thus automatically providing better quality concrete where this is possible.

4. Practical fly ash concrete for highway purposes must be resistant to freezing and thawing damage. It has been found that the necessary dosage of air entraining agent to assure such resistance varies with fly ash and replacement percentage, but can be predicted from results of the Foam Index Test. This is a simple test that can be readily carried out by field personnel.

5. Fly ash concretes batched to the same slump level were found to exhibit smaller VeBe times and gave qualitative indications of superior placeability and finishability as compared to the reference plain concretes without fly ash.

6. The results indicate that set retardation may be expected for fly ash concretes in general, and the extent of retardation is likely to be greater for high calcium fly ashes than for low calcium fly ashes.

7. The heat build-up during the early stage of cement hydration is significantly lower for fly ash concretes than for plain concretes, but the effect is less pronounced for high calcium fly ashes.

8. The values for static Young's modulus and for Poisson's ratio recorded for the fly ash concretes tested were well within the normal range for plain portland cement concretes.

9. It was found that the Poisson's ratio for the fly ash concretes tested was strongly and linearly correlated with Young's modulus, but the specific relationship found was different from that usually reported

for plain portland cement concrete. The slope is greater and the relationship is linear to very high modulus values, unlike that of plain portland cement concrete.

10. Close linear relationships were found between both Young's modulus and Poisson's ratio and compressive strength. For both relationships, the slope was higher than usually found with plain concretes, and the relationships were linear to the highest strength values achieved, approximately 6,000 psi.

11. It was found that the dynamic modulus of elasticity of fly ash concretes were initially lower than those of plain concretes, but matched or exceeded the plain concrete values after 28 days.

12. Fly ash concretes designed according to the CPQ method were found to have compressive strengths comparable to plain concretes after 3 days, and to generally exceed their compressive strengths by 90 days.

13. The flexural strengths of the fly ash concretes were slightly lower than those of plain concretes at all ages, although the differences were minimal by 180 days. The high calcium fly ashes yielded somewhat better flexural strengths than the low calcium fly ashes.

14. Flexural strength development in plain concrete was found to vary significantly with the specific cement used, but these differences were almost eliminated when fly ash was incorporated.

15. Pore size distribution curves for mature fly ash cement pastes were found to be somewhat different from those of plain cement pastes. In general, the mean size of the distributions was finer, and extra pore space was detected in the finest size ranges, indicating that

a greater volume of cement gel may be present.

16. Chloride permeability tests carried out on mature concrete specimens indicated that the fly ashes all significantly reduced the chloride permeability. The effect was greater for low calcium fly ashes, and for higher levels of cement replacement.

17. Freezing and thawing tests indicated that fly ash concretes batched with appropriate levels of air entraining agent so as to maintain a 6% air void content were all durable to freezing and thawing.

18. Pore solutions expressed from mature fly ash cement pastes were found to have significantly reduced levels of alkalies and hydroxide ions, with the reduction in alkali ions primarily confined to potassium. A reduced risk of alkali aggregate reaction should result.

19. Fly ash cement pastes were found to bind admixed chloride somewhat more effectively than plain cement pastes, thus reducing the risk of steel corrosion.

20. Results of measurements of calcium hydroxide contents in pastes for ages up to 1 year showed that little pozzolanic reaction had occurred. The calcium hydroxide contents found were generally equivalent to that predicted for the same cement diluted with an inert material in the same proportion as that of the fly ash. This result was unexpected, and not in accordance with the usual picture of fly ash reaction in concrete.

21. Scanning electron microscope studies confirmed that most fly ash spheres, even after a year, showed only modest indications of having reacted, generally showing only light surface etching. This

reinforces the previous conclusion drawn from calcium hydroxide analyses. In many cases relatively unreacted fly ash spheres were near to or surrounded by calcium hydroxide deposits, showing that failure to react more extensively was not due to a local shortage of calcium hydroxide.

22. Non-evaporable water contents of fly ash pastes were higher than predicted for the same cements diluted with chemically inert material in the same proportion as the fly ash used. This is apparently due to additional hydration of the cement present as compared to that in the plain cement pastes.

23. In general, fly ash used in properly designed concrete was found to improve most properties of the concrete, especially at later ages. Improvements were noted for both low calcium and high calcium fly ashes, but to different degrees with different properties. All of the fly ashes tested would produce satisfactory concrete for field use. The benefits derived seemed not to result from pozzolanic reaction but from some other mechanism or mechanisms, since almost no pozzolanic reaction was detected even after one year.

13.0 GENERAL RECOMMENDATIONS CONCERNING THE USE OF FLY ASH IN HIGHWAY CONCRETE

13.1 Introduction

In this final Chapter we attempt to provide recommendations and suggested guidelines for the practical use of fly ash in highway concrete. These recommendations are based in part on the experimental work reported here, and in part on other information derived from the experience of ourselves and others as reported in the technical literature.

13.2 Selection and Specification of Fly Ash

The results obtained in the present research suggest that all of the five representative fly ashes tested would be satisfactory for use in field concrete, if the concrete were properly designed and controlled. We believe that in general most fly ashes would be reasonably satisfactory on the same basis. Our experience with 14 Indiana fly ashes studied in the previous project is that only one is clearly unsuited for use in concrete, although several others are probably marginal.

The ASTM specifications with respect to selection of fly ash provide some, although limited, protection against the use of inappropriate fly ash materials. In the absence of reported information on previous performance of a given fly ash, selection should certainly be restricted to those ashes that meet all of the specification requirements.

In selecting the specific fly ash to be used for a given project, emphasis should be placed on choosing a fly ash which has shown only limited variations in its properties over time. Records are kept by reliable fly ash producers and brokers that detail the test results obtained from the given source over long periods of time. If at all possible, selection should be made from among the available fly ashes with such a track record.

All other things being equal, fly ash derived from a modern, efficient combustion plant is likelier to be more uniform and provide fewer problems than fly ash derived from an older plant. Base load operation of the plant is a definite plus.

With respect to a choice between Class F (low calcium) and Class C (high calcium) fly ashes, it appears from our present results and those of many others, that both can be satisfactory, and that neither rates a clear overall preference per se. Class C fly ashes do tend to react faster, but Class F fly ashes produce excellent strength if sufficient time is allowed, and have certain advantages with respect to durability considerations. For example, as shown in the present work, the reduction in chloride permeability value is significantly greater for Class F fly ashes than for Class C fly ashes. Similar results have been reported by others.

13.3 Concrete Mix Design

The method of concrete mix design developed in this research is a procedure specifically tailored to field application with emphasis on reproducible well-controlled production of durable highway concrete. In particular, the maintenance of the selected water:cement + fly ash ratio is automatically enforced, regardless of variations in the water demand induced by fly ash variations. This is not possible in most mix design procedures, which are usually aimed at insuring a minimum level of concrete strength. Thus with most methods adequately strong concrete of poor durability can routinely be batched, or alternatively, uneconomically high cement factors may result from the mix design calculations.

However, we do not recommend that this new method be used exclusively or without regard to prior practice. Certainly if local history of the successful use of a given fly ash in concrete designed with one of the other methods is available, future use of the same design method ought to be satisfactory. If other methods are to be used, we recommend one of the modified replacement methods rather than either simple replacement or one of the so-called "rational" methods.

However the final mix design is arrived at, we believe that it is important to provide a larger amount of fly ash per unit volume of concrete than the amount of cement deleted from the mix. We see this "over-replacement" as providing very inexpensive insurance against lower strength and poorer durability that may result in practice from a too small content of cement, especially at early ages.

With respect to the percentage of fly ash to incorporate in highway concrete, we feel that restraint is called for by the nature of the exposure that such concrete undergoes. While satisfactory high strengths can be obtained with concretes of high fly ash replacement levels using selected fly ashes, the requirement of most highway concrete for relatively early strength development and development of resistance to deterioration would suggest that very high fly ash concretes are generally inappropriate. This is particularly true for concrete used in repair and rehabilitation of existing highways, where the demand for rapid opening of the facility to traffic is always present. Also, fly ash concrete placed late in the construction season in climates like that of Indiana require more rapid assurance of the development of maturity than can usually be provided with very high fly ash replacement levels.

Another factor that should be mentioned in this connection is adequate curing. Highway concrete is generally not cured very well; a too thin application of an inadequate curing compound is more common than not, and high fly ash content concrete is particularly vulnerable to such inadequate provision for curing.

Based on the above considerations and our own experience, we feel that fly ash concrete for highway purposes should rarely exceed a fly ash replacement level of 25%, and should almost never exceed 30% unless a very superior fly ash is used and stringent job controls are in place.

In some of the existing literature, the concept of an "optimum" fly ash replacement level has been introduced. In part this is related to the idea of a cement efficiency factor for fly ash. In our experience, there is no such thing as an optimum replacement level for all properties of fly ash concrete of interest; higher levels may be superior for certain properties (for example, reduction of chloride permeability) while lower levels are superior for others (for example, development of flexural strength). The selection of a replacement level is thus a task involving the balancing of various effects, as conditioned by the type of concrete being designed, the exposure, the specific fly ash, and considerations of economy.

In highway applications, admixtures other than air entraining agents are not universally employed, but adequate air entrainment is an absolute necessity for freeze-thaw durability. Since fly ashes do generally affect the dosage of air entraining agent required to produce an adequate air void system, it is absolutely necessary to test that the amount of admixture being used will in fact provide a sufficient air content. The required amount of air entraining agent with a given fly ash concrete can easily be established using the simple Foam Index test. We recommend that such testing always be done at the start of a new project, and periodically during the course of major projects, and furthermore that accurate air void content measurements be insisted upon during the course of construction.

Admixtures other than air entraining agents are being developed by various commercial producers specifically for fly ash concrete, and certainly use of such admixtures should be encouraged in highway concrete where they lead to technically superior concrete at a reasonable cost premium.

13.4 Likely Effects of Fly Ashes on Field Processing Behavior of Concrete

One of the general observations developed over our experience is that fresh fly ash concrete, designed for a given slump value, appears more coherent (dryer and less workable) than corresponding plain concrete at the same slump. However, such appearance is deceptive; usually such concrete will require less water and be more, rather than less, workable. There is a natural tendency among concrete producers to want to add water because the concrete appears too dry; this should be resisted at all costs.

Properly designed fly ash concretes should show less bleeding than plain concretes, and should develop almost no segregation. Because of the relative lack of bleeding, finishing operations can usually start earlier. On the other hand, some fly ashes retard set severely enough that finishing operations should not be undertaken too early. Failure to take this into account and beginning finishing operations too soon for retarded concretes may result in sealing in some of the limited amount of bleeding water near the surface, thus creating a weak zone near the surface that renders the concrete subject to future problems. In such cases one would expect to start the finishing operations somewhat later than is usual for plain concrete.

Most highway pavements are placed and finished by paving trains, and it is wise to be aware that fly ash concrete may handle somewhat differently than plain cement concrete, and some adjustment of paving train operations may be required. In general, we expect that fly ash concrete should be easier to finish, and therefor a greater rate of progress may be expected.

Occasionally some high calcium fly ashes may induce a premature stiffening akin to false set, which can produce problems in practical paving operations. If recognized early, the problem can be eliminated by special admixtures, or by altering the mixing cycle (remixing). In extreme case a different fly ash may have to be used.

In general, as indicated earlier, appropriate curing of fly ash concrete is somewhat different from what is usually practiced with plain concrete. In many cases curing should be started earlier, without waiting for any bleeding to be developed; however, in general, greater care needs to be taken that the curing compound and dosage used are adequate to retain enough moisture in the concrete for curing to proceed properly.

13.5 Expected Effects of Fly Ash On Strength Gain

Our results and those of others indicate that with properly designed fly ash concrete, while some set retardation is to be expected, the rate of development of compressive strength may be expected to be little different than with plain portland cement concrete. This is especially true with Class C fly ash of good reactivity.

One caution needs to be mentioned here. The results obtained in the usual laboratory study, including the present project, reflect strength development under the usual room or laboratory temperature conditions. It is usually appreciated that for ordinary concrete the rate of development of compressive strength is reduced at lower temperatures, and highway construction in late fall is usually restricted accordingly. With fly ash concrete, one should expect both set retardation and delays in early strength gain to be disproportionately more severe at low temperatures, and plan construction operations accordingly.

Even at "normal" temperatures, our results suggest that the development of flexural strength in fly ash concrete lags that of plain concrete to a greater extent than does the development of compressive strength. While no data are at hand, we would expect that at low temperatures this effect would be even more pronounced. Where specifications call for attainment of a specified level of flexural strength before new construction can be opened to traffic, as is the case in Indiana, the possible additional delay when using fly ash concrete should be planned for and operational planning adjusted to take this into account.

Our data, and those of others, indicate that strengths and other mechanical properties of properly designed fly ash concretes eventually equal, and usual exceed those of reference concretes after a few months. Certainly, all indications are that the potential durability of such concretes exceeds that of plain portland cement concretes. Accordingly, it should be kept in mind that the troublesome effects that we call attention to here are temporary in nature, and that one should expect generally superior service from fly ash concrete after the first few months.

Finally, we should mention that where retardation and slow strength gain with fly ash concrete constitute problems, there are several avenues of possible solution to consider. As mentioned previously, admixture manufacturers have designed accelerators to work specifically with fly ash concretes, and the use of such admixtures should be considered. Indeed, where potential steel corrosion is not a potential problem, the use of calcium chloride at moderate dosage might be considered. Another possibility is the incorporation of small amounts of silica fume along with the fly ash, with the idea being that the presence of the silica fume should increase early strength gain and compensate for the effect of the fly ash. Such combined treatments are being investigated for various purposes, and may turn out to have considerable applicability to highway concrete.

13.6 Expected Effects of Fly Ash on Concrete Durability

As mentioned previously, all of the indications obtained in the present project indicate that properly designed fly ash concrete should be more durable in service than similar plain concrete.

In general terms, provided that proper attention is paid to air entrainment, and assuming that the aggregates themselves are durable, freezing resistance should be as high with fly ash concrete as with plain concrete.

The considerably refined pore structure of the fly ash concrete should make it generally more resistant to damage induced as a result of penetration of dissolved substances from the outside. Possible alkali aggregate problems with borderline reactive aggregates should be mitigated; indeed, the use of fly ash constitutes one of the standard methods for avoiding such problems.

Resistance to steel corrosion, especially chloride-induced steel corrosion, should certainly be higher.

About the only potential problem that could be negatively affected by the use of some fly ashes is sulfate attack. A few Class C fly ashes have been implicated in causing increased sensitivity to sulfate attack, although this particular problem has not been the source of any major difficulty in Indiana and most surrounding states. Where local external conditions are such that the concrete might be expected to come into contact with heavily sulfate bearing ground water, prior testing of the fly ash to be used for resistance to sulfate attack should be carried out, or a Class F fly ash substituted.

13.7 Sources of Technical Assistance

In this section we call attention to the existence of a number of potential sources of technical information and assistance concerning fly ash properties and the use of fly ash in concrete, for the benefit of engineers who may need assistance or specific information. This list is not meant to be complete, but we hope it may be helpful in practical terms.

The best general source of current information on fly ash in concrete is the state of the art report by Committee 226 of the American Concrete Institute, "Use of Fly Ash in Concrete." This report was published in the Sept.- Oct. 1987 issue of the ACI Materials Journal (Volume 84, No. 5) and is also available separately from the American Concrete Institute, Box 19150, Redford Station, Detroit MI 48219-0150.

Specifications for fly ash for use in concrete are provided by the American Society of Testing and Materials (ASTM) under the designation C 618, "Standard Specification for Fly Ash and Raw or Calcined Natural Pozzolan for Use as A Mineral Admixture in Portland Cement Concrete". This specification is under revision.

The trade association of producers and distributors of fly ash is the American Coal Ash Association, 819 H St., Washington, D. C. They can supply information on fly ash production, and on potential uses in a variety of applications.

A major organization involved in research and promotion of the use of fly ash is the Electric Power Research Institute (EPRI), 3412 Hillview Avenue, Palo Alto, CA 94303.

Individual fly ash marketing firms, many of them active in many states or internationally, are useful sources of information and many have attained a high degree of expertise with respect to applications of fly ash in concrete.

The Coal By-Products Utilization Laboratory of the University of North Dakota, Grand Forks ND 58202 has been active in providing assistance and analytical services in connection with fly ash utilization.

For a number of years the Materials Research Society has sponsored annual symposia on fly ash utilization, including some work on concrete applications. The published symposia volumes are available from the Materials Research Society, 9800 McKnight Road, Pittsburgh, PA 15237.

A number of individual research symposia on fly ash in concrete have been held by organizations such as the American Concrete Institute, ASTM, and the Transportation Research Board. Individual proceedings are available from these organizations.

Two recent books devoted entirely to the use of fly ash in concrete are "Fly Ash in Cement and Concrete" by R.A. Helmuth (published by the Portland Cement Association, 5420 Old Orchard Road, Skokie, IL 60077 in 1987 and "Fly Ash in Concrete" by E.E. Berry and V. M. Malhotra, published as Special Publication 85-3 by the Canada Centre for Mineral and Energy Technology in 1986. The latter volume is available from the Canadian Government Publishing Centre, Supply and Services Canada, Ottawa Canada K1A 0S9.

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